

October, 1936

RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER DIVISION of the AMERICAN CHEMICAL SOCIETY



VOLUME IX

NUMBER 4

MICRONEX BEADS

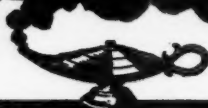
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RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, C. W. Christensen, Easton, Pennsylvania, or The Rubber Service Laboratories Co., Akron, Ohio.

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Rubber Division Activities

The Rubber Division of the American Chemical Society

Officers

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Executive Committee..	N. A. SHEPARD, R. H. GERKE, W. F. BUSSE, J. T. BLAKE, E. B. BABCOCK
Sergeant-at-Arms.....	L. V. COOPER

The Rubber Division Meeting in Pittsburgh, Pennsylvania, September 10-11, 1936

The meeting was held in the Hotel Roosevelt, with approximately two hundred seventy-five in attendance. The following papers were presented:

1. H. F. Jordan, P. D. Brass, and C. P. Roe. Examination of Latex and Latex Compounds. I. Physical Testing Methods.
2. D. E. Fowler. Examination of Latex and Latex Compounds. II. Chemical Testing Methods.
3. H. B. Townsend. Production and Properties of Vulcanized Latex.
4. L. A. Wohler. Physical Testing Procedure for Latex Stocks.
5. H. W. Greenup and L. E. Olcott. Preparation and Properties of Latex Battery Separators.
6. W. F. Bixby and E. A. Hauser. The Transparency of Rubber Compounds Containing Magnesium Carbonate.
7. C. R. Boggs and J. T. Blake. Deproteinized Rubber.
8. Robert T. Sheen, H. Lewis Kahler, and Delbert C. Cline. Determination of Sulfur in Rubber.
9. David Craig. The Determination of Diarylamines in Rubber Compositions.
10. Thomas Midgley, Jr., and Albert L. Henne. Natural and Synthetic Rubber. XVII. Sol Rubber and Gel Rubber.
11. Ira Williams. The Structure of Rubber Sols as Indicated by Swelling and Viscosity Measurements.
12. John T. Blake. Unsaturation of Rubber Vulcanized with Dinitrobenzene.
13. M. W. Harman. The Vulcanization Characteristics of Certain Mercapto-benzothiazole Derivatives.
14. E. W. Booth and D. J. Beaver. An Air Bomb Aging Test for Tread Compounds.
15. M. F. Torrence. The Effect of Cure and Temperature on Flex-Cracking.

The Banquet was held Thursday evening, September 10, in the Hotel Roosevelt, with three hundred forty in attendance.

The Division wishes to thank the following companies for the very fine table favors which they furnished: Binney and Smith; Godfrey L. Cabot, Inc.; Columbia Alkali Corporation; General Atlas Carbon Company; Herron and Meyer;

J. M. Huber, Inc.; Monsanto Chemical Company; Naugatuck Chemical Company; New Jersey Zinc Company; United Carbon Company; R. T. Vanderbilt Company.

It was decided that the one nominated for Vice-Chairman but not elected automatically becomes a member of the Executive Committee.

The Chairman appointed the following nominating committee for new officers: S. M. Cadwell, Garrett Barnes, Jr., H. W. Greenup, L. M. Freeman.

The following officers were elected for the coming year: *Chairman*, H. Trumbull; *Vice-Chairman*, A. R. Kemp; *Secretary-Treasurer*, C. W. Christensen; *Sergeant-at-Arms*, L. V. Cooper.

Executive Committee: N. A. Shepard, R. H. Gerke, W. F. Busse, J. T. Blake, E. B. Babcock.

The Chairman announced that the Institution of the Rubber Industry in England extended to the members of the Rubber Division an invitation to attend an International Conference in the early summer of 1938. It was voted that the new Chairman appoint a Committee to decide the Division's attitude toward the proposed meeting of the Institution.

The resignation of W. A. Gibbons as a member of the Crude Rubber Committee was accepted, and R. H. Gerke was appointed his successor.

The Crude Rubber Committee report was read and accepted.

The Executive Committee voted that the Rubber Division is to meet with the National Society in the spring of 1937 at Chapel Hill, North Carolina.

Secretary's Report

Total Membership to September 8, 1936.....	485
Members paid for 1936.....	388
Associate members paid for 1936.....	97
New Members and Associate Members for 1936 (included in above figure).....	65
Total Members not paid for 1936.....	36
Subscriptions paid for 1936.....	122
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It was also decided that it is hereafter the duty of the Vice-Chairman to submit all papers received for future meetings to the various reviewers.

C. W. CHRISTENSEN, *Secretary-Treasurer*

New Books and Other Publications

Memento de L'Industrie du Caoutchouc. (Directory of the Rubber Industry.) In French. By F. Jacobs. Published by Société d'Éditions Techniques Cillard, 49 Rue des Vinaigriers, Paris, France. 444 pp. 70 Francs (in the United States).

This valuable reference book is published as part of the *Encyclopédie du Caoutchouc et des Matières Plastiques*. It consists of seven chapters on (1) accelerators, (2) retarding agents, (3) antioxidants, (4) colors and pigments, (5) plasticizers and solvents, (6) emulsifying and stabilizing agents, and (7) synthetic rubbers and plastics. The materials are listed in alphabetical order, and wherever possible the trade names, manufacturers in various countries, the selling agents in France, the chemical formulas, physical properties, and recommended uses are given. A general alphabetical index, as well as the addresses of the principal manufacturers are included. This handbook with its 434 pages, exclusive of the index, is exhaustive and up-to-date, carefully arranged and concisely worded. It should prove of much aid to all rubber compounders and technologists, since it gives information on the properties and characteristics of the numerous chemicals and raw materials used in rubber goods manufacture. An American chemist can therefore now obtain in France a book containing more information about American products than can be found in any American publication. [G. G. HAWLEY.]

Rubber—A Story of Glory and Greed. By Howard and Ralph Wolf. Published by Covici-Friede, Publishers, 432 Fourth Avenue, New York City. 526 pp. \$4.25.

Written by two capable co-authors, both of them former newspapermen, one of them a graduate of chemical engineering and an active rubber chemist, this book represents the story of rubber translated into the words of the layman. It traces the growth of the rubber industry from the days before its actual "discovery" by Columbus up to the current year, with each event and development written in a style entertaining, readable, and instructive. The authors make free use of a word-lash in depicting the manner in which financiers and promoters reaped the rightful awards of pioneers and scientists. The extensive research essential to the compilation of a book of this character is reflected in each chapter. Personalities, whose names are indelibly stamped in the rubber industry, are treated throughout the book. The problems of marketing, price wars, threatened monopoly and labor are told in an interesting style, with sidelights cast by the authors as to possible solutions. The book concludes with an account of the larger rubber companies of today, with complete details of their financial, production, and labor policies. Every individual associated with the rubber industry should enjoy reading this work. [From *The Rubber Age* of New York.]

Draft British Standard Methods for the Analysis and Testing of Latex and Rubber. This mimeographed proposal (48 pages and 88 figures) has been prepared by the British Standards Institute at the request of the Research Association of British Rubber Manufacturers and is now being circulated for comment. Copies of the proposal may be obtained from the American Standards Association, 29 West 39th St., New York, N. Y. The proposal includes sections on analysis and testing of latex, methods of chemical analysis of rubber, methods of testing soft vulcanized rubber, and methods of testing hard rubber. [From the *India Rubber World*.]

An Outline of Malayan Agriculture. Compiled by D. H. Grist, agricultural economist, Department of Agriculture, Straits Settlements and Federated Malay States, Kuala Lumpur, 1936. Cloth, 388 pages, 5 $\frac{3}{4}$ by 6 inches. Indexed. Two maps and 86 plates. Price \$3.

This book retains a few of the features of its predecessors, but has been entirely rewritten to present a picture of Malayan agriculture in 1935. The work classes rubber as first of the five major crops and will be of considerable value as a concise compendium for the planter, agriculturist, student, administrator, and those in search of general information. [From the *India Rubber World*.]

The Vanderbilt Rubber Handbook—1936. Seventh Edition. Edited by W. F. Russell. Published by R. T. Vanderbilt Company, 230 Park Avenue, New York City. 280 pp.

Both in physical appearance and editorial contents, this latest edition of the Vanderbilt Handbook differs materially from the preceding volumes. Rather than in the loose-leaf binding of past years, it is bound in book form, with a serviceable cloth cover. As for its contents, the book is devoted to practical facts and figures rather than theoretical discussions, with theory kept in the background as much as possible. A certain amount of historical material has also been introduced in this issue, "in view of the fact that in recent years there has appeared an increasing interest in the past development of the rubber industry," according to the foreword. The latest edition of the Handbook is split into three sections, i. e., Vanderbilt materials, general articles and tables, and useful data, with each of the three sections easily distinguishable by the use of different color paper stock. In addition, there is a very informative section on "Building Rubber Compounds," by Paul I. Murrill and L. A. Edland, covering the aims of rubber compounding, materials, building up a rubber compound, and the compounding of latex. Among the interesting general articles are those dealing with raw rubber, specifications, hard rubber, electrical properties of rubber, sulfur determination, physical testing, latex, water dispersions, yarn, and fabric testing, etc. By far, this edition is the best ever issued by Vanderbilt. It should prove invaluable to every rubber technologist. [From *The Rubber Age*, New York.]

Organic Plastics. Gordon M. Kline. Circular of the National Bureau of Standards C 411 issued May 16, 1936. Paper, 27 pages, 6 by 9 inches. United States Government Printing Office, Washington, D. C. Price 5¢.

This circular presents a summary of information assembled regarding those organic plastic materials of chief industrial significance, including the raw materials required, the chemical reactions involved, the various methods of processing, and the more important applications. The organic plastics are divided into four principal groups for discussion: namely, the synthetic resins, the natural resins, the cellulose derivatives, and the protein substances. The synthetic resins are subdivided into several chemical types as follows: phenolic-aldehydic, amino-aldehydic, vinyl, hydroxy-carboxylic, indene, organic-polysulfides, and miscellaneous. Natural resins of animal, vegetable, and mineral sources are described. The chemistry of the cellulose esters and ethers and cellulose xanthate is outlined. The protein plastics considered include those prepared from casein, blood albumin, and soy beans. Selected references are listed at the conclusion of the circular for the convenience of the reader who may be interested in further details regarding the manufacture, properties, and uses of organic plastics. [From the *India Rubber World*.]

Farm Tractor Tire Handbook. The B. F. Goodrich Co., Akron, Ohio.

This thirty-page book of pocket size has as its object the distribution of information concerning the advantages of rubber tires on farm power units in agri-

culture and transportation. Fourteen pages are devoted to relating just what type of jobs rubber tires have handled more efficiently than any other method. Eight pages record tire specifications, load and inflation table, tractor tire and wheel specifications, and industrial tractor specifications. Servicing of low pressure tires in the field, including the subjects of weights, chains, and blocking the tractor for best work, take up several pages. The various types of service for rubber tires on the farm are pictured. [From the *India Rubber World*.]

Goodrich Load and Inflation Pressure Table for Trucks and Buses. The B. F. Goodrich Co., Akron, O. In addition to inflation pressures a load and service diagram is given illustrating the effect of overloading on the ultimate service of a pneumatic tire. [From the *India Rubber World*.]

The Chemists' Year Book for 1936. Eighteenth Edition. Founded by F. W. Atack, Edited by E. Hope, Sherratt & Hughes, 34 Cross St., Manchester, England. Chemical Publishing Co. of N. Y., 148 Lafayette St., New York, N. Y., exclusive agents for North and South America. Cloth, 1257 pages, 4 $\frac{1}{4}$ by 6 $\frac{1}{4}$ inches. Indexed. Price \$6.

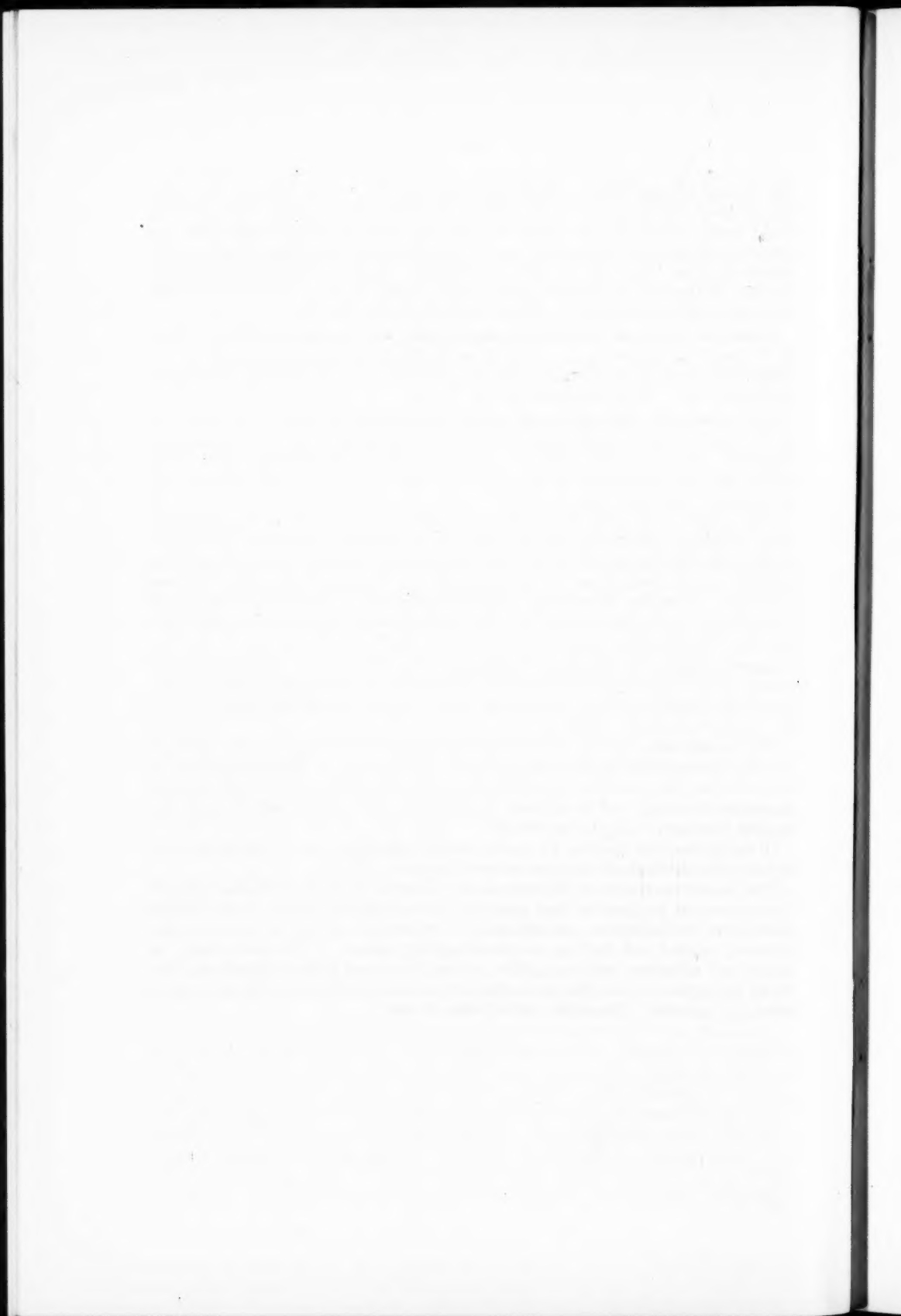
This handbook is practically a full reference library of chemistry and technology, with tabulated data on properties, methods of analysis, logarithmic tables, etc. In short this eighteenth edition has been thoroughly revised and includes much new material on "General Properties of Inorganic and Organic Compounds," "Essential Oils," "Tanning Materials," "Leather Analysis," "Dairy Products," and "Alkaloids;" and a new section on "The Analysis of Sulphuric Acid Treated Oils, Alcohols and Wetting Agents." [From the *India Rubber World*.]

Annual Survey of American Chemistry. Vol. X. 1935. Edited by Clarence J. West. Published for the National Research Council by Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y. 1935. Cloth, 487 pages, 5 $\frac{1}{2}$ by 8 $\frac{1}{2}$ inches. Indexed. Price \$5.

With this volume the Annual Survey completes the first decade of its existence, the ten volumes covering the period 1925 to 1935, inclusive. During this time an endeavor has been made to cover, as completely as possible, the progress made in American chemistry and to indicate the trends in the various fields of pure and applied chemistry in the United States.

Of the 25 chapters this year 12 are devoted to industrial topics. This is the same as last year, although the subjects covered are quite different.

The chapter on rubber by Webster Jones, Carnegie Institute of Technology, reviews chemical progress in that industry in the following order: crude rubber, plasticizers, vulcanization, and structure of vulcanized rubber, accelerators, ages-resistors, control and testing, compounding ingredients, rubber technology, cements and adhesive, reclaiming, hard rubber, latex and rubber dispersions, synthetic rubber and rubber-like products, derivatives of rubber, miscellaneous processes, and patents. [From the *India Rubber World*.]



The Effect of the Conditions of Drying on the Aging Properties of Sheet Rubber

J. D. Hastings

PART I

Previous Work

The successive operations in the preparation of sheet rubber may be regarded as stages in a manufacturing process, the object of which is the removal of water from latex and production of dry rubber in a form easily handled and shipped. The last stage in this process is concerned with the drying of wet machined sheets. In order that the time required to dry the sheet shall not be unduly prolonged, the sheets are dried at temperatures higher than normal, and usually in some form of smoke-house. Smoke-drying has been used since the very earliest days of the industry, and was started as an attempt to imitate the smoke-drying of thin films of latex in the preparation of fine hard Para, when plantation rubber had not established its market. Its use has persisted, however, and has in fact several advantages, but it is not unreasonable to believe that other methods of drying could be devised which would eliminate entirely the need of smoking.

Considerable quantities of firewood are used in the smoke-drying of sheet rubber. In anticipation of a serious shortage of firewood in rubber-producing countries, several investigations concerned with the possibility of its elimination have been made. Eaton¹ investigated the utilization of wood in Malaya in 1924. He considered that it might be possible to substitute unsmoked for smoked sheet, since smoking is not advantageous so far as the intrinsic vulcanization properties of the rubber are concerned. Unsmoked sheet may be even superior when dried at very slightly elevated temperatures. O'Brien² considered alternative methods of sheet preparation in Ceylon on account of the serious shortage of firewood which was feared, and prepared a number of samples of sheet air-dried under different conditions, together with corresponding smoked sheet controls. These samples were examined in the laboratories of the London Advisory Committee for Rubber Research. The results showed that the air-dried sheet was invariably inferior in aging properties to the smoked controls, particularly when dried at temperatures above 90° F. All the air-dried sheet, however, was made from latex to which *p*-nitrophenol had been added to prevent mold development in the dry sheet; it was suggested that this might account for the inferior aging, and further experiments were made. As a result of these tests O'Brien³ states that sheet, without *p*-nitrophenol and air-dried at 100° F., has better aging properties than the smoked sheet controls, whereas that containing *p*-nitrophenol is distinctly inferior. Martin⁴ states that, although drying sheet in smoke is a relic of the days when fine hard Para was more widely used, it does appear to make the rubber more plastic and to prevent mold development. He states, however, that there is no intrinsic difficulty in drying sheet in air at somewhat higher temperatures, that this improves plasticity and decreases mold development, and that air-dried sheet is a comparatively new product, the demand for which is believed to be increasing.

The necessity for the strictest economy in the plantation industry during recent difficult times has compelled the producer to consider very carefully any alterations or improvements which may reduce costs in the process of preparation. Improved designs for new smoke-houses and attention to ventilation systems, with slight structural alterations in many of the present smoke-houses of the older type, have effected considerable reductions in the time required to dry sheet rubber. A drying period of four days is now quite common in Malaya, and there are few estates today taking ten days or more to dry their sheet, a period considered quite normal a few years ago. Recent developments have been directed towards reducing the time of drying still more, and there are some estates in Malaya equipped with the latest type of driers, in which sheet is dried regularly in two days. The temperatures used for rapid drying are, of course, considerably higher than those used in smoke-houses of previous days, and in general the sheet is much lighter in color. The air-dried and smoked sheet prepared by O'Brien (*loc. cit.*) for his aging comparisons was dried at temperatures lower than those in general use today, and it was also dried more slowly. In view of this tendency to speed up the drying process, it is pertinent to enquire whether the intrinsic properties of rubber are affected by these alterations in drying conditions.

Experimental

The accelerated aging test used in these experiments was the well-known Bierer-Davis oxygen bomb test. The details of the test adopted are given below.

Mixing.—The standard mixture was 20 grams of sulfur and 200 grams of rubber.

Curing.—The mixtures were kept for 24 hours, after which they were cured in molds in a steam autoclave at 149° C.

Time of Cure.—The mixtures were cured for a time sufficient to give a load of approximately 0.80 kg. per sq. mm. at an elongation of 890 per cent. This point represents a time of cure about 20 minutes shorter than the arbitrarily chosen optimum. The cure taken as optimum in these experiments was that which gives a curve passing through the point, elongation 890 per cent, load 1.30 kg. per sq. mm. As intervals of less than five minutes were not considered in the vulcanization process the cure adopted for aging may have been sometimes 15, 20, or 25 minutes shorter than the optimum.

Aging Conditions.—Schopper rings were aged in a bomb at an oxygen pressure of 300 lbs. per sq. in. and a temperature of 60° C. for periods of 24, 48, and 72 hours. All rings were kept for 24 hours at atmospheric temperature after removal from the bomb before testing on a Schopper tester. Four rings were broken in each case to obtain an average result for tensile strength.

The oxygen pressure and temperature were those normally used in bomb-aging, but the state of cure of the mixings before aging was an arbitrary one. It was adopted here from a consideration of aging tests made to ascertain at what state of cure differences in the aging properties of various rubbers could best be distinguished.

It was found that there was considerable difference in the aging of rubber from different estates when tested under the conditions described above, and that hot-air-dried sheet appeared to age more poorly than smoked sheet.

A comparison was then made of the aging properties of hot-air-dried and smoked sheet prepared from the same latex in an identical manner up to the drying stage. The preparation of the wet sheet was that given to our standard acid controls which are prepared in the following manner: Field latex is diluted to 1.5 lbs. per gallon dry rubber content and coagulated in pans with 1 per cent formic acid at

the rate of 7.5 fluid ounces per gallon of latex. The coagulum is machined the following morning and passes through the machines five times, four times through the smooth and once through the marking rolls. It is then soaked in running water for two hours, drained for two hours, and dried.

The air-dried sheet was dried in an electrically heated, thermostatically controlled drying cabinet and the smoked sheet was dried in a neighboring estate smoke-house. The time of drying was three and four days at temperatures of 120–130° F. and 120–140° F., respectively. The aging results are given in Table I.

TABLE I
SMOKED AND AIR-DRIED STANDARD CONTROL SHEET
Vulcanized Rings Aged in Oxygen at 300 Lb. per Sq. In. Pressure
Temperature 60° C.

Sample	Time of Cure to Give 1.30 Kg. per Sq. Mm. at an Elongation of 890%, Min.	Aging Cure Min.	Tensile Strength after Aging for Hours: Kg. per Sq. Mm.			
			0	24	48	72
Hot-Air-Dried Sheet	102	80	1.26	1.26	0.79	0.06
Smoked Sheet	104	85	1.13	1.27	1.26	1.24

TABLE II
SHEET PREPARED UNDER STANDARD CONDITIONS
Vulcanized Rings Aged in Oxygen at 300 Lb. per Sq. In. Pressure
Temperature 60° C.

Sample No.	D.R.C., Lb. per Gallon	Air-Dried Sheet or Smoked Sheet	Time of Cure to Give 1.30 Kg. per Sq. Mm. at an Elongation of 890%, Min.	Aging Cure, Min.	Tensile Strength after Aging for Hours: Kg. per Sq. Mm.			
					0	24	48	72
L 194/1/1	2 1/2	Air-Dried Sheet	98	75	1.28	1.48	1.28	0.35
L 195/1/1	1 1/2	Air-Dried Sheet	109	95	1.34	1.34	0.15	0.03
L 196/1/1	1 1/2	Air-Dried Sheet	103	85	1.48	1.34	0.79	0.07
L 194/1/2	2 1/2	Smoked Sheet	108	90	1.29	1.38	1.24	1.13
L 195/1/2	1 1/2	Smoked Sheet	109	95	1.30	1.49	1.31	1.15
L 196/1/2	1 1/2	Smoked Sheet	125	105	1.32	1.34	1.28	0.57

TABLE III
SHEET PREPARED FROM COAGULUM SOAKED FOR 24 HOURS BEFORE MACHINING
Vulcanized Rings Aged in Oxygen at 300 Lb. per Sq. In. Pressure
Temperature 60° C.

Sample No.	D.R.C., Lb. per Gallon	Air-Dried Sheet or Smoked Sheet	Time of Cure to Give 1.30 Kg. per Sq. Mm. at an Elongation of 890%, Min.	Aging Cure, Min.	Tensile Strength after Aging for Hours: Kg. per Sq. Mm.			
					0	24	48	72
L 194/1/3	2 1/2	Air-Dried Sheet	101	85	1.41	1.34	0.86	0.06
L 195/1/3	1 1/2	Air-Dried Sheet	106	90	1.34	1.34	0.80	0.06
L 196/1/3	1 1/2	Air-Dried Sheet	110	90	1.43	1.19	0.08	0.05
L 194/1/4	2 1/2	Smoked Sheet	95	95	1.27	1.45	1.32	1.01
L 195/1/4	1 1/2	Smoked Sheet	90	90	1.21	1.36	1.28	1.18
L 196/1/4	1 1/2	Smoked Sheet	105	105	1.36	1.45	1.08	0.13

TABLE IV
SHEET PREPARED FROM LATEX COAGULATED WITH EXCESS ACID
Vulcanized Rings Aged in Oxygen at 300 Lb. per Sq. In. Pressure
Temperature 60° C.

Sample No.	D.R.C., Lb. per Gallon	Air-Dried Sheet or Smoked Sheet	Time of Cure to Give 1.30 Kg. per Sq. Mm. at an Elongation of 890%, Min.	Aging Cure, Min.	Tensile Strength after Aging for Hours: Kg. per Sq. Mm.			
					0	24	48	72
L 194/2/1	2 1/2	Air-Dried Sheet	112	90	1.30	1.35	1.16	0.10
L 195/2/1	1 1/2	Air-Dried Sheet	113	90	1.31	1.36	1.08	0.09
L 196/2/1	1 1/2	Air-Dried Sheet	117	95	1.35	1.25	0.48	0.05
L 194/2/2	2 1/2	Smoked Sheet	116	95	1.31	1.44	1.38	1.24
L 195/2/2	1 1/2	Smoked Sheet	117	100	1.36	1.48	1.32	1.04
L 196/2/2	1 1/2	Smoked Sheet	124	105	1.39	1.31	0.97	0.08

TABLE V
SHEET PREPARED FROM LATEX COAGULATED WITH EXCESS ACID, COAGULUM SOAKED
24 HOURS BEFORE MACHINING
Vulcanized Rings Aged in Oxygen at 300 Lb. per Sq. In. Pressure
Temperature 60° C.

Sample No.	D.R.C., Lb. per Gallon	Air-Dried Sheet or Smoked Sheet	Time of Cure to Give 1.30 Kg. per Sq. Mm. at an Elongation of 890%, Min.	Aging Cure, Min.	Tensile Strength after Aging for Hours: Kg. per Sq. Mm.			
					0	24	48	72
L 194/2/3	2 1/3	Air-Dried Sheet	111	90	1.48	1.42	0.80	0.06
L 195/2/3	1 1/2	Air-Dried Sheet	114	95	1.34	1.22	0.61	0.07
L 196/2/3	1 1/2	Air-Dried Sheet	118	100	1.34	1.36	0.07	0.05
L 194/2/4	2 1/2	Smoked Sheet	119	100	1.44	1.42	1.35	1.09
L 195/2/4	1 1/2	Smoked Sheet	119	100	1.24	1.26	1.12	0.88
L 196/2/4	1 1/2	Smoked Sheet	126	105	1.32	1.43	1.24	1.20

TABLE VI
DETAILS OF DRYING CONDITIONS

Sample No.	Air-Dried Sheet or Smoked Sheet	Where Dried	Time of Drying, Hours	Temperature of Drying, ° F.	Color of Dry Sheet
L 251/1	Air-Dried Sheet	R. R. I.	92	120-130	Light yellow
L 251/2	Smoked Sheet	Estate A	144	120-130	Brown
L 251/3	Smoked Sheet	Estate B	64	120-130	Blue-black
L 251/4	Smoked Sheet	Estate C	92	120-140	Brown
L 251/5	Smoked Sheet	Estate D	72	130-140	Brown
L 251/6	Smoked Sheet	Estate E	43	130-145	Orange-brown
L 251/7	Smoked Sheet	Estate F	264	130	Light orange

TABLE VII
STANDARD SHEET DRIED IN DIFFERENT SMOKE-HOUSES
Vulcanized Rings Aged in Oxygen at 300 Lb. per Sq. In. Pressure
Temperature 60° C.

Sample No.	Air-Dried Sheet or Smoked Sheet	Where Dried	Time of Cure to Give Load of 1.30 Kg. per Sq. Mm. at Elongation of 890%, Min.	Aging Cure, Min.	Tensile Strength after Aging for Hours: Kg. per Sq. Mm.			
					0	24	48	72
L 251/1	Air-Dried Sheet	R. R. I.	115	95	1.25	1.28	0.34	0.05
L 251/2	Smoked Sheet	Estate A	120	100	1.23	1.19	1.33	0.99
L 251/3	Smoked Sheet	Estate B	126	105	1.24	1.43	1.31	1.34
L 251/4	Smoked Sheet	Estate C	120	100	1.41	1.25	1.29	1.20
L 251/5	Smoked Sheet	Estate D	118	100	1.28	1.33	1.23	0.63
L 251/6	Smoked Sheet	Estate E	124	100	1.31	1.45	1.26	0.14
L 251/7	Smoked Sheet	Estate F	115	95	1.27	1.25	0.09	0.05

The rate of deterioration of the air-dried sheet was greater than that of the smoked sheet. Similar results were obtained when other direct comparisons were made with sheet dried in hot air and in smoke.

An experiment was then carried out in which sheet was prepared from one crop of latex diluted to different dry rubber contents before coagulation, and dried in the hot-air cabinet and the estate smoke-house as before. The preparation of the sheet, up to the drying stage, from latex diluted to various strengths was that adopted as standard for the particular D.R.C. and differs only from that given to standard sheet in the quantity of acid used and number of machinings given to the coagulum. The aging results of the sheet are given in Table II.

The smoked sheet prepared from latex coagulated at all three dry rubber contents aged better than the corresponding air-dried sheet. That prepared from latex of low D.R.C., however, did not appear to retain its tensile strength so well as that prepared from latex of higher D.R.C.

Air-dried and smoked sheet was also prepared from the same latex diluted similarly, but from coagulum which was soaked for 24 hours before machining. The aging figures given in Table III again show smoked sheet ages better than air-dried sheet.

In connection with other experiments, further samples of air-dried and smoked sheet were made from this same bulk of latex under similar conditions, except for the amount of acid used for coagulation, which was 50 per cent more than normal. Aging tests were carried out, and the results for sheet made under normal conditions and after the coagulum had soaked for 24 hours are given in Tables IV and V.

Smoked sheet is superior to air-dried sheet in all experiments in which the rubber was prepared from latex of D.R.C. 2.5 and 1.5 lbs. per gallon. With very dilute latex of 0.5 lb. per gallon D.R.C., the smoked sheet was not superior in all cases, though the rate of deterioration was not quite so fast as for the corresponding air-dried samples.

Sheet Dried in Estate Smoke-Houses.—An experiment was made to ascertain whether sheet prepared and hot-air-dried at the Institute was inferior to that prepared at the Institute and dried in estate smoke-houses other than the particular house used for the smoke-drying of the sheet tested in the previous experiments. A number of standard control wet sheets were prepared at the Institute from the same crop. Some were hot-air-dried and some taken to a number of estates where they were dried in the estate smoke-houses by kind permission of the managers. There was considerable variation in the type of smoke-house in which these sheets were dried, and the dry rubber differed in color from house to house. The details concerned with the drying of these sheets are given in Table VI and the aging results in Table VII.

As was expected, the air-dried sheet showed poor aging, but it is also to be noted that rubber dried in different smoke-houses varied in its aging resistance. As a rough classification it may be said that these sheets fell into two groups having good and poor aging properties. The sheet dried on Estates A, B, and C had good aging properties, while that from D, E, and F had inferior aging properties, Estate F being particularly poor.

Discussion

Apart from the values in Table VII, which are discussed separately, the results indicate that sheet dried in hot air, in a time commensurate with modern drying practice, is invariably inferior in aging properties to that dried in smoke, unless

the latex be diluted to a low D.R.C. before coagulation. Since in these experiments the sheet was made from the same latex and in an identical manner up to the drying stage, it is evident that the smoking process improves the aging properties. It may be argued that the results in Table VII are not in accordance with this conclusion. An examination of Table VI giving the conditions under which the sheet was dried is of considerable interest in this connection, and an explanation of the anomalies is suggested. Estates A, B, and C, which produce sheet with satisfactory aging properties, have smoke-houses which are of the older type but which dry rubber in a reasonable time. Sheet dried in these houses was brown, that dried on Estate B being particularly dark. Estates D and E, which fall into the group which gave inferior aging, have rapid-drying houses of a patented design, and sheet dried in these houses is not dried in smoke through the whole drying period. Their construction is such that after an initial period of smoke-drying the operation is finished in a hot-air chamber without smoke at a more elevated temperature. Estate F, which gave sheet with aging inferior even to that of sheet dried in hot air, has an old type of smoke-house, but it will be observed that the time of drying was much longer than any of the other estates. On inquiry into the reason for this, it was found that the sheet was actually dry in a shorter time, but the color was so light that it was left in the smoke-house a longer time to darken. It was still, however, very light even after 11 days' drying. The possibilities of impairing the aging properties by prolonged heating are at once apparent.

Until more information is available on a number of points which are now under investigation, it is not proposed to suggest any explanation for the differences in aging properties between hot-air-dried and smoked sheet. Experiments concerned with the effects of different preparation treatments at different dilutions, in conjunction with variations in time and temperature of drying, are in progress. Further experiments concerned with the humidity at which drying takes place and time during which the sheet is in an atmosphere of smoke will give information from which more definite conclusions on the effect of the drying conditions on the aging properties may be drawn.

Summary

An examination of sheet rubber prepared in identical manner up to the drying stage shows that hot-air-dried sheet and smoked sheet have different aging properties.

Hot-air-dried sheet is invariably inferior to smoked sheet, except when prepared from very dilute latex. Further work is required before any explanation is offered.

Acknowledgment

The preliminary work of my late colleague, Dr. Wiltshire, on the aging properties of clonal and estate rubber led him to express the opinion that it was impossible to compare aging properties unless the details of preparation were known and that they would most likely determine the aging properties. The work described in this paper developed from these ideas, and grateful acknowledgment is made.

Thanks are due to the managers of the various estates who kindly coöperated in the drying experiments, and particularly to the manager of Kepong Estate who has so kindly permitted us to use his factory on many occasions.

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The Surface Composition of the Rubber Globules in Hevea Latex

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The latex of *Hevea brasiliensis* consists of rubber globules suspended in a serum containing proteins, so-called rubber resin (*i. e.*, acetone-soluble substances) and methylinositol, together with smaller quantities of sugars and saline substances. The resin of rubber has been shown by Whitby, Dolid, and Yorston¹ to consist mainly of unsaturated fat acids together with other fat acids and sterols. As mentioned later, the protein and fat acids possibly may be partly in some form of association.

The colloidal properties of the latex will depend largely upon the amounts of the capillary-active substances (*i. e.*, mainly proteins and resin) adsorbed at the surface of the rubber globules. The influence of the protein on the behavior of latex appears first to have been recognized by Weber.² Although Weber made his investigations with Castilloa latex and, contrary to present ideas, regarded the rubber in the latex globules as incompletely polymerized, his views on the existence of a surface film of protein steadily received wider acceptance, and it was early realized that they would apply also to the case of Hevea latex (which today is of paramount importance), although not to all natural latices generally.

This extension of the original observations was clearly stated by de Vries.³

The rubber resin on the other hand, judging by the experiments of Freundlich and Hauser,⁴ of Scholz,⁵ and of de Vries and Beumée-Nieuwland,⁶ has little influence on the stability or behavior of Hevea latex. Subsequently, however, Beumée-Nieuwland⁷ has postulated the presence of an adsorbed lipid layer in addition to the adsorbed protein. This theory has been further elaborated by Belgrave⁸ and van Rossem,⁹ who assume the adsorption of a lipid-protein complex.

The recent rapid extension of latex processes for rubber manufacture involving the need for initial stabilization of Hevea latex, and later adjustment of its stability to various degrees as necessary for different methods of use, renders desirable as exact knowledge as possible of the character of the active protective substances in commercial latex.

The object of this paper is to describe the experimental determination of the fractions of the exposed surface of the rubber globule composed of protein and rubber resin. The method employed is based on the assumption that the resultant surface-charge density of a composite colloidal particle depends on the surface-charge densities of the capillary-active substances adsorbed at the particle surface, and on the fractions of the surface area occupied by those substances. In the case of the globules in Hevea latex, the rubber hydrocarbon surface is more or less occupied by a covering of protein or fat acid character. Thus if f_p , f_F be the fractions of the surface covered with protein and with rubber resin, respectively, f_R be the fraction of uncovered rubber surface, and σ_p , σ_F , σ_R be the surface-charge densities of the protein, resin, and rubber surfaces, respectively, then it is assumed that the resultant surface-charge density of the latex globule will be

$$\sigma = \sigma_p f_p + \sigma_F f_F + \sigma_R f_R \quad (1)$$

or,

$$\sigma - \sigma_R = (\sigma_p - \sigma_R)f_p + (\sigma_F - \sigma_R)f_F \quad (2)$$

It has previously been shown (Kemp¹⁰) that the relation between the cataphoretic mobility of a particle and its surface-charge density can be satisfactorily expressed by the equation of Henry,¹¹

$$u = \frac{\sigma}{\eta} \cdot \frac{\kappa a}{1 + \kappa a} f(\kappa a) \quad (3)$$

where u denotes the cataphoretic mobility, σ the surface-charge density, η the coefficient of viscosity of the solution, a the radius of the particle, κ is proportional to the square root of the ionic strength, and $f(\kappa a)$ is a function of κa . It follows from equation (3) that when the value of κa exceeds 100, the variation of mobility with particle-size is, for the present purposes, negligible, and in this case the mobilities of different particles are proportional to their surface-charge densities.

Thus equation (2) becomes

$$(u - u_R) = (u_p - u_R)f_p + (u_F - u_R)f_F \quad (4)$$

where u , u_p , u_F , u_R are the cataphoretic mobilities of particles of latex-rubber, of protein, of resin, and of rubber hydrocarbon, respectively.

The values of these different mobilities will depend on the ionic environment of the particles. Thus, in one particular environment we have

$$(u' - u_R') = (u_p' - u_R')f_p + (u_F' - u_R')f_F \quad (5)$$

and in a second environment, providing f_p , f_F remain unchanged,

$$(u'' - u_R'') = (u_p'' - u_R'')f_p + (u_F'' - u_R'')f_F \quad (6)$$

Since the values of the mobilities in the two cases are readily determined by experiment, the value of f_p and f_F can be calculated.

In practice, the method was applied by determining the mobility- p_H relations in buffer solutions of ionic strength 0.01 for particles of pure rubber hydrocarbon, of protein, of resin, and of latex-rubber. The value of κa was in no case less than 150, so that the effect of small variations in the particle size could be neglected.

Experimental

The measurements of electrophoretic mobility were made with a micro-cataphoresis apparatus of the capillary-tube type, in conjunction with a slit ultra-microscope. Determinations of p_H were made by means of an antimony electrode.

Rubber Hydrocarbon.—Crepe rubber was extracted with acetone for 96 hours to eliminate the resin. The rubber was then dissolved in chloroform and emulsified with alcohol and water containing caustic soda, the final concentration of alkali being approximately normal. The emulsion was repeatedly shaken with fresh quantities of caustic soda solution to free the rubber from proteins. The emulsion was finally washed until the p_H of the washings was less than 8. The emulsion was then stabilized with a little ammonia, the p_H being 9, and shaken vigorously with water. The aqueous dispersion of purified rubber was then boiled under reduced pressure to remove the volatile solvents. The properties of the rubber dispersion were not affected by this boiling, since similar mobility values were obtained with dispersions from which the solvents had been removed by aeration.

The results for the dispersion of the rubber hydrocarbon are shown in Fig. 1, Curve 3. It will be seen that as the p_H is decreased, the negative charge on the

rubber globules falls, owing to the adsorption of hydrogen ions, and finally the charge becomes zero at $p_H 2.4 \pm 0.1$.

The Protein of Latex.—Ammonia-preserved plantation latex of 35 per cent con-

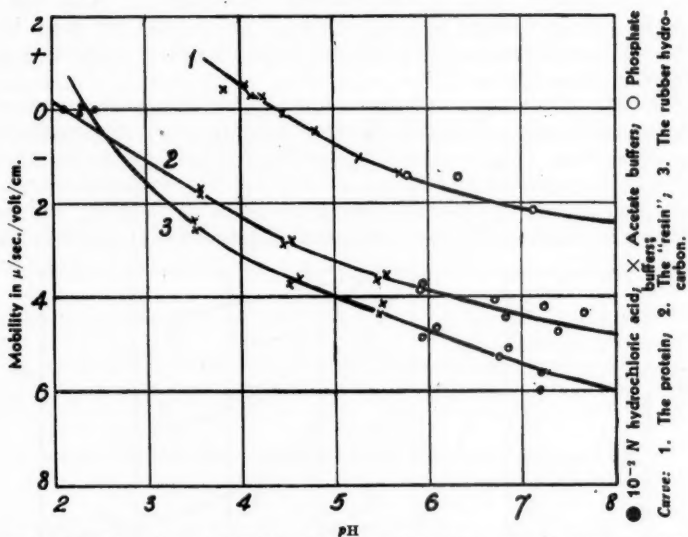


Figure 1—Constituent Colloids of Latex in Solutions of Ionic Strength 0.01

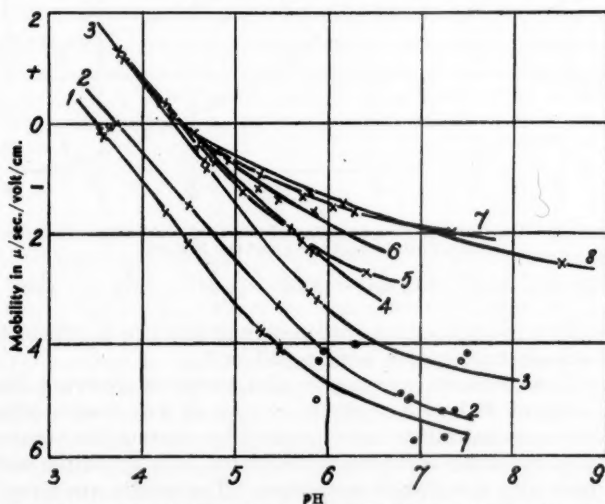


Figure 2—Diluted Plantation Latex in Solutions of Ionic Strength 0.01. \times Acetate Buffers; \circ Phosphate Buffers

Curve	Concn. of Latex (Per Cent).
1	0.0016
2	0.0098
3	0.39
4	1.18
5	3.91
6	6.76
7	8.98
8	19.5

centration was coagulated by dilute acetic acid, and the clear filtered serum was saturated with ammonium sulfate to precipitate the protein. The precipitate was filtered off, redissolved in acid of $p_H 2.0$, and reprecipitated with ammonium

sulfate. The precipitate was collected, dissolved in water, and excess of electrolyte was removed by electro dialysis.

In order to determine the cataphoretic mobility of the protein, it was necessary to make measurements with protein-covered silica particles, since the protein does not give sols containing visible particles. The results are given in Fig. 1 (Curve 1). The isoelectric point of the protein or mixture of proteins in the solutions employed is $p_H 4.40 \pm 0.07$.

Rubber Resin.—The acetone solution of resin obtained in the preparation of rubber hydrocarbon was mixed with distilled water to give a dispersion of rubber resin, excess acetone being removed by aeration. The mobility- p_H relation for resin particles is expressed as Curve 2 of Fig. 1. The negative charge on the particles is due in part to the ionization of the acids in the resin, and partly to ionic adsorption. Thus, as the p_H is decreased, ionization of the acids is repressed,

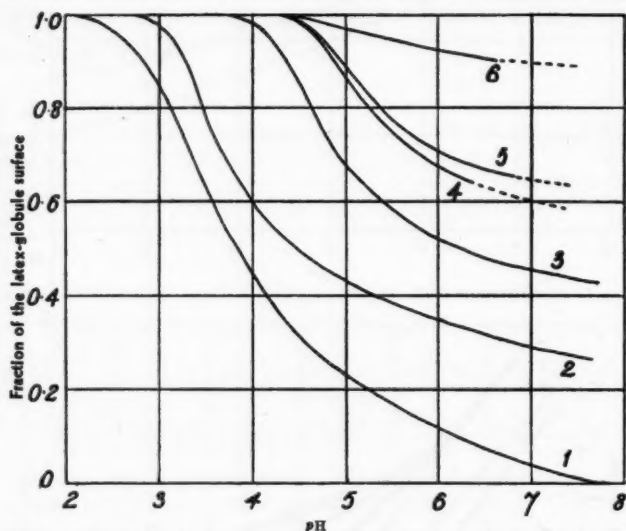


Figure 3—Relation between Fraction of the Globule-Surface Covered with Protein and the p_H of the Serum

Curve	1	2	3	4	5	6
Latex	0.0016	0.098	0.39	1.18	3.91	6.76
Concn. (Per Cent)						

and in sufficiently acid solutions adsorption of hydrogen ions is sufficient to reverse the charge, the isoelectric reaction being $p_H 2.1 \pm 0.1$.

The Latex.—Measurements were made with ammonia-preserved Hevea latex, of total solid content 39.1 grams per 100 cc., about five months after tapping. Latices of various concentrations were prepared by diluting this plantation latex, and, in the case of the higher concentrations of latex, ionic impurities were removed by electro dialysis with a collodion membrane. The results are given in Fig. 2. From the graphs it will be seen that the cataphoretic behavior of latex depends on the degree of dilution.

Both the slope of the mobility- p_H curve and the isoelectric point of the latex dispersion depend on the latex concentration. For low concentrations of latex, it was possible to make measurements over a large p_H range, but for higher concentrations, the measurement of mobility became difficult in solutions of $p_H > 7$, since usually in such solutions no aggregation of latex globules took place, and

owing to the large number of globules present, the intensity of reflected and diffracted light was too great for convenient observation.

Discussion

The slopes of the mobility- p_H curves for latex of low concentrations are appreciably greater than those for rubber hydrocarbon, protein, and resin, indicating that the amounts of protein and of resin on the rubber surface may change continuously with p_H . Thus the solubilities of these two substances increase with p_H , and consequently in highly diluted latex, the rubber particles may be quite uncovered in alkaline solutions (Fig. 2, Curve 1).

In acid solutions (p_H about 4) Curves 3, 4, 5 of Fig. 2 indicate mobilities which are somewhat greater than those given by the protein curve (Fig. 1, Curve 1). There is thus a slight discrepancy from the theory, since it would be expected that the slopes of the curves for latex would begin to fall on the acid side of the isoelectric points.

As the latex concentration is increased, the mobility- p_H curve approaches more nearly that of protein, showing that the fraction of the globule surface covered with protein increases as the concentration of protein increases. The curves for the highly diluted latex do not, therefore, obey the equation for the mobility- p_H slopes

$$\left(\frac{du}{dp_H} - \frac{du_R}{dp_H}\right) = \left(\frac{du_p}{dp_H} - \frac{du_R}{dp_H}\right)f_p + \left(\frac{du_F}{dp_H} - \frac{du_R}{dp_H}\right)f_F \quad (7)$$

hence the values of f_p and f_F cannot be derived from substitution in equations (5) and (6).

However, by a method of successive approximations, the values of f_p and f_F for the "average" latex globule at a given p_H can be calculated. At a particular p_H , the values of u , u_p , u_F , u_R can be measured, and, in addition, the approximate values of f_p and f_F can be obtained from the measured values of the mobilities, since near the isoelectric point, when the latex curve approaches the protein curve, we assume

$$f_p \doteq \frac{u - u_R}{u_p - u_R} \text{ and } f_F = 1 \doteq f_p,$$

and by substituting these values in the equation (7), it is possible to obtain the theoretical value of du/dp_H at the p_H of measurement, since the slopes of the other curves are known at this p_H . From the approximate equation (7) and the more exact equation (4), the values of f_p and f_F can be obtained. The mobilities in equation (4) are correct to ± 5 –7 per cent, the slopes substituted in equation (7) are measurable to ± 10 –15 per cent, and the approximate values of f_p and f_F can be calculated to ± 10 per cent near the isoelectric point. The errors in the final values of f_p and f_F vary with the p_H for the lower concentrations of latex, but do not exceed ± 10 per cent at p_H 7. The errors are greater in the case of Curves 1 and 2 of Fig. 2, where the protein covering appears to be incomplete at the isoelectric point.

By this method the change in the surface composition of the average rubber globule in latex with varying p_H could be obtained. The results are shown in Figs. 3 and 4.

In Fig. 5 is shown the variation in the surface composition of the average rubber-globule at p_H 8.0 as a function of the concentration of latex. It will be noted that the extreme surface of the average rubber globule is entirely composed of protein

at this p_H when the concentration has risen to about 12 per cent of total solids. Hence, the outer surface of the rubber globules in ordinary undiluted Hevea latex

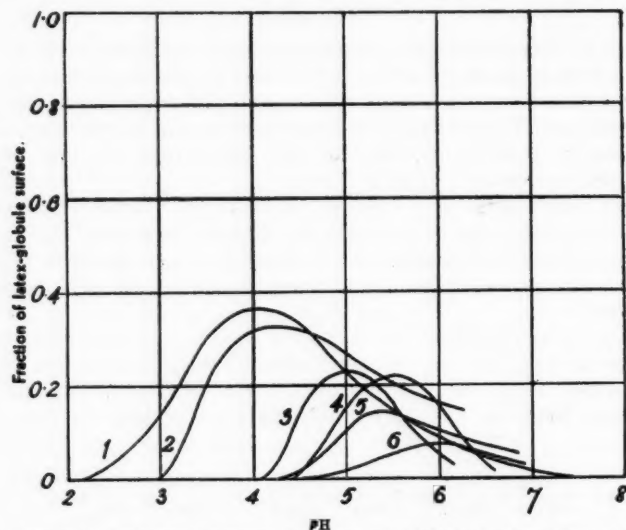


Figure 4—Relation between Fraction of Globule-Surface Covered "with Rubber Resin" and the p_H of the serum

Curve	Latex	Concn. (Per Cent)	1	2	3	4	5	6
			0.0016	0.098	0.39	1.18	3.91	6.76

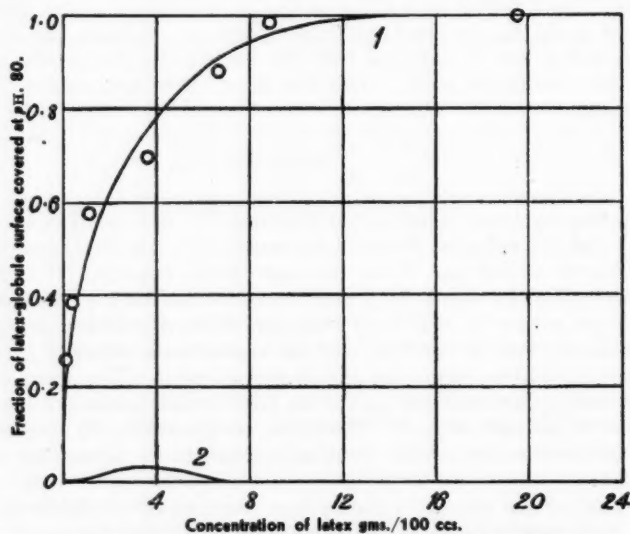


Figure 5—Variation in Surface Composition of Rubber Globule at p_H 8.0 with Dilution of the Latex. 1. Protein. 2. Resin.

at p_H 8.0 is entirely of protein character, and the slope of the f_p - p_H curve indicates that they are still completely covered at the p_H of the preserved latex, i. e., p_H 10.

Similarly, it is evident that the rubber globules in ammonia-preserved 60 per cent latex (obtained by centrifugal creaming of ordinary plantation latex) are also completely covered with protein.

It should be noted that these results are not necessarily at variance with the possible presence of the protein as a lipid-protein complex, though they agree more naturally with the simpler view as to the independence of the protein and the rubber-resin.

Summary

1. A method for the surface analysis of colloidal particles is outlined.
2. The electrophoretic behavior of the protein, resin, and rubber hydrocarbon of the latex of *Hevea brasiliensis* is described.
3. The electrophoretic behavior of diluted ammonia-preserved plantation latex has been investigated, and it is shown that the amounts of protein and rubber resin adsorbed at the surface of the rubber globule depend on the degree of dilution of the latex and on the p_H of the serum.
4. The fractions of the rubber-globule surface covered with protein and with rubber resin are calculated, and their variation with latex-dilution and the p_H of the serum is plotted.
5. The rubber globules at p_H 8.0 are completely covered with a protein layer, provided the latex is not diluted below 12 per cent of total solids.

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Rubber. XVII

Detection of Methylglyoxal and the Ozone Cleavage of Rubber

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1. INTRODUCTION

Since the work of Harries, the question whether methylglyoxal is found in the ozone cleavage of rubber has played an important part in explaining the constitution of this hydrocarbon. Since Harries found no methylglyoxal, he assumed a cyclic formation of isopentene, $\text{—CH}_2\text{C}(\text{CH}_3)\text{:CH.CH}_2\text{—}$, residue and the absence of a corresponding $\text{—CH:C}(\text{CH}_3)\text{.CH:CH}_2$ end group, which would necessarily yield methylglyoxal. Nevertheless, in view of the probability that a very long open chain is present in the rubber molecule, the necessity again arose of trying to identify methylglyoxal as a product of the ozone cleavage. This involved the problem of detecting extremely small quantities, since the length of the chain might be very great. Provided that no secondary reaction takes place, the yield of methylglyoxal, if formed, should give information about the length of the chains. If, for example, in the cleavage 0.1 per cent of the carbon skeleton were to appear as methylglyoxal, it might be concluded from the three carbon atoms that the chain length is 1000 times greater, *viz.*, 3000 carbon atoms, or 600 isoprene units. These investigations have been undertaken as a conclusion of our earlier work on the ozone cleavage of rubber, in which approximately 90 per cent of the cleavage products were obtained as compounds of the levulinic aldehyde (acid) series.

2. PRELIMINARY EXPERIMENTS ON THE SEPARATION OF METHYLGLYOXAL AND LEVULINIC ALDEHYDE

(Part A of the Experimental Work)

Aside from the ozone cleavage, the chief problem was naturally to determine methylglyoxal quantitatively in the presence of levulinic aldehyde, acetaldehyde, and formaldehyde, a problem which is encountered in the cleavage of other natural products, and therefore is of general importance. The separation of acetaldehyde and formaldehyde is relatively simple, since their derivatives are easily soluble, for example, their dinitrophenylhydrazones can be easily separated by hot alcohol in a Soxhlet apparatus from the dinitrophenylosazone of methylglyoxal. In the case of levulinic aldehyde, however, this method is not at all successful. Although dinitrophenylhydrazine is the best reagent for the quantitative determination of methylglyoxal, in this case recourse must be had to other agents in order to detect traces of methylglyoxal in the presence of large quantities of levulinic aldehyde. Since it does not react with levulinic aldehyde, nickel methylglyoxime, recommended by Neuberg, would be a suitable reagent, except for the fact that precipitation of the extremely dilute solutions, which contain only thousandth parts of methylglyoxal, was incomplete with the nickel reagent. Table I of the Experimental Section shows that 73 per cent was obtained at a concentration of 33 mg. per cc., 33 per cent at a concentration of 22 mg. per cc., 15.5 per cent at a concentration of 0.6 mg. per cc., and 3.2 per cent at a concentration of 0.4 mg. per cc. Precipitation as disemicarbazone already used by Wolf¹ and by Meisenheimer² was found to

be considerably superior. By this method a 91 per cent yield was obtained at a concentration of 1 mg. per cc. and even with 37 γ per cc. methylglyoxal could be detected qualitatively. Separation of levulinic aldehyde is also possible from the observation that on standing over night methylglyoxal reacts completely with semicarbazide, whereas precipitation of levulinic aldehyde does not take place on account of the high solubility of its semicarbazone. In this way we were able to obtain 90 per cent of the methylglyoxal formed and then to convert the filtered, but not easily characterized disemicarbazone into the dinitrophenylosazone of methylglyoxal with a yield of 95 per cent by warming with 2,4-dinitrophenylhydrazine in 17 per cent sulfuric acid, a method which has already been recommended by Neuberg for its isolation.

Because of its blue-violet solution in alcoholic potassium hydroxide, its crystalline form and its solubility, this derivative is more easily identified than is the disemicarbazone. By means of this transformation, we obtained in control tests approximately 85–87 per cent of the methylglyoxal present in extremely dilute solutions, free of levulinic aldehyde. In this connection it should be mentioned that a separation of the two ketoaldehydes was first made directly with 4-nitrophenylhydrazine. However, this method is troublesome and not quantitative (see Experimental Section).

3. RESULTS OF OZONE CLEAVAGE (Part C of Experiments)

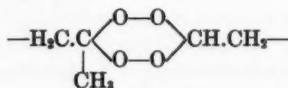
In these preliminary experiments, we used the combined semicarbazidedinitrophenylhydrazine method for the detection of methylglyoxal in the cleavage of rubber. In earlier experiments³ we had concluded from qualitative reactions that methylglyoxal is formed. In order to separate this compound from the main mass of other reaction products, it was distilled from the cleavage solution of the rubber ozonide which had been obtained with water at 80–90° C. This solution was then concentrated in a current of nitrogen in an oil bath having a descending condenser, ultimately a temperature of 140–160° C. being necessary, until no more methylglyoxal passed over. Simple heating to 100° was not sufficient. Even in our experiments, 10 per cent of the methylglyoxal remained in the cleavage solution. As a control experiment, one of us (Socias-Viñals) subjected mesityl oxide to ozone cleavage (Part B of the Experiments) in order to see to what extent methylglyoxal is formed in general in the ozone cleavage according to Harries. Our preliminary experiments were far from satisfactory, *e. g.*, in carbon tetrachloride at 15° C. the yield was only 7.4 per cent, in water 18 per cent, and in chloroform at 0°, by very careful cleavage of the ozonide with sulfurous acid, the yield rose to only 29 per cent. This is accordingly a somewhat poorer yield than the yields obtained by Fischer, Düll, and Ertel⁴ by catalytic hydrogenation cleavage of the ozonide at –20° C. (40 per cent of the crude product). Nevertheless in the beginning we continued to use in working with methylglyoxal the cautious water cleavage at 80° in a current of nitrogen which had already been used for rubber ozonide, because it made it possible to separate the methylglyoxal in a very simple way. This procedure was, however, supplemented by previous treatment with cold sulfurous acid.

The yield of methylglyoxal which we first obtained in this way was on the average 1 per cent of the carbon skeleton of the rubber. It should be pointed out, however, that such quantities of methylglyoxal are obtained only by overozonization. If the action of ozone on the chloroform solution of rubber is interrupted at the moment when the solution becomes stable to bromine, no methylglyoxal or only a very small quantity (less than 0.1 per cent) is found as a result of the cleavage. Accordingly it might be suspected that this owes its origin to a secondary action of

ozone on the rubber ozonide. Opposed to this is the fact that after a certain period of time (12 hours) the time of overozonization has no influence on the yield of methylglyoxal. After 7 hours the effect of overozonization is still small, the methylglyoxal being 0.33 per cent of the carbon skeleton; after 12, 18, 29, and 45 hours the yields remained in all cases around 1 per cent. This would be inexplicable if the final rubber ozonide were to be changed further in any way by ozone in the sense that methylglyoxal were to be formed from each isopentene group by the introduction of oxygen. As a matter of fact, it has frequently been observed, in ozone cleavages of conjugated systems of double bonds, that excess ozone is necessary for complete saturation. Frequently only one monoozonide is formed, which takes up additional ozone very slowly.⁵ There remained nothing to do therefore other than to make the best of the disadvantages involved in overozonization.

Finally, however, we succeeded in treating overozonized rubber by reduction, *i. e.*, with aqueous sulfurous acid, in such a way that no traces of methylglyoxal were formed, as was proved in the case of mesityl oxide. Concentration of any methylglyoxal which may have been formed was carried out by distillation, and in virtue of the sensitivity with which the semicarbazone can be detected (37 γ per cc.) it may be said that with 1000 isopentene groups no terminal isoprene group with a conjugated system can be present.⁶ Scheibe and Pummerer have already come to a similar conclusion as a result of their work on the absorption spectrum of rubber; for 500 isoprene groups examined—probably also for 1000—no isoprene group was found. As is known, Staudinger is of the opinion, as a result of viscosity measurements, that a very long isopentene chain $[-CH_2.C(CH_3):CH.CH_2-]_x$ is present in rubber where x is greater than 1000, perhaps even 2000. On the basis of the formation of methylglyoxal, which may be avoided completely by means of suitable operating conditions, this view cannot be challenged.

The result of the ozone decomposition even supports to some extent the results of both physical methods. However, on the whole it is an unsettled question how the ends of long chains are actually formed, and whether the unsaturated groups which we have endeavored to detect are actually present. In the case of polystyrene also, this question is still unsolved from a chemical point of view. Secondary reactions in the case of ozonide cleavages, with formation of water, have frequently been observed. In our case it is noteworthy that with any overozonization, though not to the saturation point of ozone, a maximum of 1 per cent of methylglyoxal is obtained. A secondary reaction to the extent of 1 per cent can be assumed, which does not take place in the cleavage of the normal ozonide, but only in the water cleavage of the alkalidene peroxide:



though not in this cleavage with sulfurous acid.⁷ Of course it is also conceivable that ozonides of conjugated systems react with sulfurous acid in an abnormal manner. As a preliminary step, we first examined experimentally the hypothesis of a secondary reaction, and we found that methylheptenone as well, which should yield no methylglyoxal, does actually yield this compound, in similar amount and even under similar conditions, that rubber does. Accordingly, a secondary reaction involving ozone cleavage seems very probable in the case of rubber.

Gutta-percha, which differs from rubber sterically, shows a behavior strictly analogous to that of rubber with respect to ozone cleavage; thus no methylglyoxal is formed except with overozonization or with overozonization and treatment with

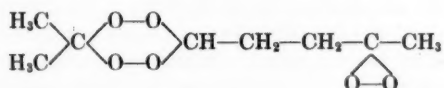
sulfurous acid. With overozonization and cleavage with water at 80° C., approximately 1 per cent of methylglyoxal is obtained.

In these experiments acetaldehyde was also found among the products of ozonization of rubber and of gutta-percha, but its origin is still not clear (Experiment, page 567).

4. COMPARATIVE EXPERIMENTS WITH METHYLHEPTENONE

(Braun and Matthäus)

Methylheptenone was compared with rubber because it too has two double bonds in the 1,5-position, although one of these is a C:O double bond. On over-saturation with ozone, it is possible that an alkylidene peroxide of the following formula is formed:



Levulinic acid (levulinic aldehyde) and acetone must be formed in this cleavage, whereas methylglyoxal is not necessarily formed. If ozone is introduced only to the point of saturation, or if the product is overozonized and then treated with sulfurous acid, no methylglyoxal is obtained, any more than with rubber. On the contrary, if it is overozonized and then cleavage is carried out with water at 80°, from 0.6–0.8 per cent of the carbon skeleton appears in the form of methylglyoxal. Oxalic acid is detected as an additional cleavage fragment. One might be tempted to explain this by a bridging of oxygen between both CH₂ groups (perhaps after dehydrogenation), whereby in the secondary reaction acetone, oxalic acid and methylglyoxal might be formed to the extent of 1 per cent from the peroxide above. The quantity of oxalic acid actually found does not correspond exactly to the methylglyoxal, but it is still within two-thirds of the expected amount. This parallelism does not exist in the case of rubber, since here there is scarcely any oxalic acid; or at the most one-eighth of the quantity which would be equivalent to the methylglyoxal obtained. Moreover, oxalic acid is not a specific product of the secondary reaction, since with hydrogen peroxide, which is always formed in ozonide cleavage, levulinic acid can likewise form oxalic acid. That levulinic acid yields with ozone no methylglyoxal was proved both in inert as well as in aqueous media.

DESCRIPTION OF THE EXPERIMENTS

A. Development of a Suitable Method of Determination of Methylglyoxal in the Presence of Levulinic Aldehyde

The methylglyoxal required for the development of an analytical method was first prepared from dioxycetone, according to Fischer⁸ and later according to the Henze-Müller method by oxidation from acetone with selenium dioxide.⁹ In order to determine the content of methylglyoxal in the solution, it was precipitated with a 1 per cent solution of 2,4-dinitrophenylhydrazine in 17 per cent sulfuric acid at 37° C. This method, which was developed by Neuberg and Kobel,¹⁰ is an excellent one in itself, *e. g.*, it has a sensitivity of even 1 γ,¹¹ but it does not make possible the separation of levulinic aldehyde, which in our case was the object of the experiment. In the following sections our experiments with 2,4-dinitrophenylhydrazine, 4-nitrophenylhydrazine, nickel methylglyoxime, and semicarbazide are outlined. The determination of the quantity of methylglyoxal in the solution was made with 2,4-dinitrophenylhydrazine.

(1) *2,4-Dinitrophenylhydrazine*.—Since when cold the reaction proceeds rather slowly to the osazone, we allowed the reaction mixture to stand one day at 37° C. It was filtered, washed with water, then with 10 per cent sodium carbonate solution to remove any pyroracemic acid which might be present, and finally washed again, dried, and weighed. The melting point of the crude product was 294° C.; after recrystallization from pyridine-alcohol it was 312° C. (uncorrected; deflagration; cf. Neuberg and Kobel, 298° C.). The crude product still yielded soluble impurities in hot alcohol, whereas pure osazone no longer does so. With methyl alcoholic potassium hydroxide, a blue-violet color is formed. With potassium hydroxide in methyl alcohol, the dinitrophenylosazone of glyoxal gave a blue color, without going into solution, which is a very convenient method for identifying it.

Levulinic aldehyde yielded by the same method a dinitrophenylhydrazone which melted at 227° C., and which after recrystallization from dioxan melted at 228.5° C. (uncorr.). In a methyl alcoholic solution of potassium hydroxide it gave a deep red solution. Here too, as with the dinitroosazone of methylglyoxal, micro and semi-micro-analyses gave much too high carbon values because of the four nitro groups, whereas macro-analyses gave better results.

0.1338 gram		0.1476 gram substance:		0.2193, 0.2359 gram CO ₂	
				0.0465, 0.0478 gram H ₂ O	
C ₁₇ H ₁₆ N ₈ O ₈	Calcd.	C 44.35		H 3.50	
	Found	C 45.32, 45.12		H 3.89, 3.75	

Separation of methylglyoxal from levulinic aldehyde was not successful by means of dinitrophenylhydrazine, although the osazone is more soluble in ethyl acetate and alcohol than is the dihydrazone.

(2) *4-Nitrophenylhydrazine*.—With the mono-nitro compound the possibility of separation was somewhat better, yet here also the loss was too great. We used an excess of the reagent in 50 per cent acetic acid, to which the aqueous solution of methylglyoxal was added. The melting points of 4-nitrophenylosazone from methylglyoxal which are given in the literature vary greatly: 230–231° C.,¹² 277°,¹³ 291–293°,¹⁴ 299–300°,¹⁵ 300–304°.¹⁶ Our osazone was obtained by slow crystallization from pyridine-alcohol in blue red, doubly refractive needles, with melting point of 285–286° C. In one case with a freshly prepared sample we observed a melting point of 290°, which dropped after 8 days to 296° C. The various melting points suggest either polymorphism or *syn-anti*-isomerism. Methyl alcoholic potassium hydroxide and warm dilute sodium hydroxide give blue solutions, while concentrated sulfuric acid gives red solutions.

Levulinic aldehyde-bis-4-nitrophenyldihydrazone, like the 4-nitrophenylosazone of methylglyoxal, forms blue solutions in methyl alcoholic potassium hydroxide. The hydrazones of levulinic aldehyde and of acetaldehyde can be separated from the osazone of methylglyoxal in a Soxhlet apparatus by means of hot alcohol; that of levulinic aldehyde adheres to the osazone of methylglyoxal rather tenaciously. This latter is best obtained, though with losses by fractional crystallization, from dioxan.

(3) Hydroxylamine with nickel methylglyoxime has been recommended by Neuberg and Scheuer¹⁷ for the detection of methylglyoxal, and is in fact suitable for this purpose at not too low concentrations. However, a determination in very dilute solutions is impracticable with this reagent, as is evident in Table I. Accordingly this reagent had to be given up, although as might be expected it gave no precipitate with levulinic aldehyde. It is expedient to employ a very slight excess of hydroxylamine solution, *e. g.*, 15 grams of hydroxylamine hydrochloride and 18 grams of sodium acetate per 80 cc. of the original solution, of which the particular

number of cc. shown in the table were used. Only after the times of standing, likewise shown in the table, was nickel acetate added, following which the solution was allowed to stand 24 hours longer at 15–20° C. Acid reactions and elevated temperatures are unfavorable to the yield. It is advisable to wait for the transformation of the red into the stable orange colored modification of the nickel salt before filtering and washing. Nickel methylglyoxime gives yellow solutions in chloroform, which decompose rapidly when hot. If only very little methylglyoxal is present, so that there is no precipitation, a yellow color is sometimes still obtained after agitation with chloroform.

TABLE I

Total Solution (Cc.)	Concentration of Methylglyoxal in Exptl. Solution (in Gram/Cc.)	Hydroxylamine Solution (Cc.)	Time of rest (in Hours at 15–20°)	Nickel Acetate Solution (Cc.)	Nickel Methylglyoxime (Gram)	Methylglyoxal (Gram)	Yield (Per Cent of the Theoretical)
2	0.0333	1	55	5	0.1816	0.0488	73.2
3	0.0222	1	55	5	0.0820	0.0420	33.0
6	0.0222	4	24	8	0.1687	0.0453	34.0
11	0.0121	4	24	8	0.1736	0.0466	35.0
6	0.0111	1	55	5	0.0824	0.0221	33.1
17	0.0038		24	5	0.0708	0.0190	28.5
62	0.00107		24	5	0.0531	0.0142	20.9
77	0.00086		24	5	0.0484	0.0130	19.1
102	0.00065		24	5	0.0384	0.0106	15.5
122	0.00054		24	5	0.0287	0.0077	11.3
152	0.00043		24	5	0.0081	0.0022	3.2

Not only dinitrophenylhydrazine, but also semicarbazide improves the yield of methylglyoxal.

(4) *Semicarbazide*.—An excess of a ten per cent solution of semicarbazide together with sodium acetate was added to a solution of methylglyoxal and was let stand 24 hours, filtered, washed, and then weighed.

TABLE II

Experiment No.	Total Volume (Cc.)	Concentration of Methylglyoxal in the Experimental Solution (Gram/Cc.)	Semicarbazone chloride Solution (10%) (Cc.)	Disemicarbazone (Gram)	Methylglyoxal (Gram)	Yield (Percentage of the Theoretical)	Percentage of the Theoretical Yield in the Determination as the Nickel Oxime Salt at the Same Concentration as Methylglyoxal
1	5	0.0136	3	0.1605	0.0630	92.7	35
2	14	0.0048	3	7.1579	0.0620	91.2	31
3	29	0.0023	3	0.1549	0.0608	89.4	27
4	54	0.0012	3	0.1555	0.0611	90.0	22
5	79	0.00086	3	0.1532	0.0601	88.4	19
6	104	0.00065	3	0.1513	0.0594	87.4	15
7	204	0.00034	3	0.1495	0.0587	86.3	3
8	404	0.00017	3	0.1362	0.0534	78.6	..
9	61	0.00011	10	0.1582	0.0621	91.3	..

A comparison of the yields of methylglyoxime in the last column of Table II with the next to the last column shows the superiority of the semicarbazide method. The melting point of our product was 254° C. (uncorr.)¹⁸ after resolution in large

quantities of hot water, which gave small crystals in good condition for analysis. To convert the semicarbazone into methylglyoxal, 2,4-dinitrophenylosazone which is more easily characterized by its solubility and the color of its solutions in alcoholic potassium hydroxide, 0.1544 gram of semicarbazone were mixed with 50 cc. of a 1 per cent solution of 2,4-dinitrophenylhydrazine in sulfuric acid (10 per cent by volume) and heated a short time. By displacement of the semicarbazone residues, there was obtained 0.3472 gram of osazone, corresponding to 0.0578 gram of methylglyoxal (calculated 0.0606 gram) or a yield of 95.4 per cent.

Analysis of the crude product. 0.0132 gram substance: 2.82 cc. N (16°, 745 mm.)
 $C_{15}H_{12}O_6N_8$. Calcd. N 25.9. Found N 24.8.

In the case of the semicarbazone products prepared from rubber, this transformation was carried out to make identification more certain. The sensitivity of the 2,4-dinitrophenylosazone precipitation corresponds to 1 γ of methyl alcohol per cubic centimeter of methylglyoxal.

In order to test the sensitivity of the semicarbazone precipitation, three solutions of methylglyoxal, having concentrations of 125, 74, and 37 γ per cc., respectively, were each mixed with 5 cubic centimeters of a 10 per cent solution of semicarbazide in acetic acid, which were then made up to total volumes of 300, 500, and 1000 respectively. Experiment 1 was definitely positive after 3 hours, Experiment 2 after 18 hours, while only a slight precipitate was formed in Experiment 3 after 2 days. Therefore 37 γ is approximately the limit of sensitivity. This result was of importance in connection with the discussion of the negative course of experiments on rubber, Nos. 22-26 (see page 567).

B. Comparative Experiments with Mesityl Oxide (Socias-Viñals)

Freshly distilled mesityl oxide was used in all the experiments, because it is very easily altered, and then leads to partial resinification in the cleavage reaction. The ozone content of the current of oxygen was 1.2-1.5 per cent.

(1) 0.47 Gram of mesityl oxide was dissolved in 40 cc. of purified chloroform and ozonized at 0° C. to the point of saturation. The solution was then covered with 100 cc. of water at 0° C., thoroughly shaken, and a rapid stream of sulfur dioxide gas was passed through to mix the layers thoroughly. After standing over night in an ice box, the mixture was heated to boiling, and after cooling an excess of a solution of dinitrophenylhydrazine in 17 per cent sulfuric acid (10 per cent by volume) was added. It was then allowed to stand for 2 days, after which the chloroform was eliminated in a vacuum. The precipitate was filtered off on a glass filter, and then extracted with hot 94 per cent alcohol in a Soxhlet apparatus. There was thus obtained as an alcohol-soluble portion 1.0156 grams of product, which was predominantly acetone-dinitrophenylhydrazone; as an alcohol-insoluble portion 0.612 gram of methylglyoxal dinitrophenylosazone, corresponding to 0.102 gram of methylglyoxal or 29 per cent of the calculated quantity, which corresponds to 50 per cent of the carbon skeleton.

(2) 0.390 Gram of mesityl oxide was dissolved in 30 cc. of carbon tetrachloride and was ozonized to 15° until it was stable to bromine. It was then treated with water and sulfurous acid, as described above. It gave 0.842 gram of an alcohol-soluble portion, 0.125 gram of an alcohol-insoluble portion, *i. e.*, methylglyoxal dinitrophenylosazone, corresponding to 0.0208 gram of methylglyoxal, or 7.4 per cent of the calculated amount.

(3) Ozone was passed through 4.25 grams of mesityl oxide dispersed in 50 cc. of ice-cold water. In 24 hours the oil dissolved. An excess of sulfur dioxide was

allowed to react for one hour, after which the osazone precipitated, giving 3.461 grams of alcohol-insoluble osazone, which corresponds to 0.576 gram of methylglyoxal, or 18.5 per cent of the calculated quantity.

C. Ozone Cleavage of Rubber (Matthäus)

(1) *Preparation of Rubber Ozonide*.—Rubber solutions prepared, with the exclusion of moisture, in purified chloroform (distilled in nitrobenzene) were treated in three ways at 0° as before with a mixture of ozone and with oxygen containing a predetermined quantity of ozone: (1) until stable to bromine, (2) until just before they became stable to bromine, and (3) with ozonization of the solutions, after they became stable to bromine, for different lengths of time. The chloroform solution of the ozonide was freed from the solvent after different periods of storage in an ice box, in a vacuum and finally, in high vacuum, at 20–25° C. On longer standing and with overozonization, there was a considerable separation of levulinic peroxide. In a few experiments the chloroform which had previously been distilled was tested for methylglyoxal, and a receiver for dinitrophenylhydrazine was installed. There were found only traces of a precipitate, which however was not the osazone sought.

(2) *Cleavage of Rubber Ozonide*.—The ozonide residue was gradually warmed with a little distilled water (20–100 cc.) on a water bath with a descending condenser connected with the cleavage flask, and a current of nitrogen was passed through the liquid. The greater part of the cleavage took place at 80–90° C., after which the flask was placed on an oil bath and the methylglyoxal distilled over, the oil bath finally reaching a temperature of 160° C. In comparative experiments, it had already been proved that otherwise methylglyoxal passes over very incompletely. The methylglyoxal solution was collected in the ice-cooled receiver, with a slow and steady stream of nitrogen passing through the cleavage flask. It still contained acetaldehyde and levulinic aldehyde, both of which distill with greater difficulty than does methylglyoxal. Beyond this first receiver one or two other ice-cooled receivers were inserted containing the precipitation reagent (mono- or dinitrophenylhydrazine, hydroxylamine hydrochloride-sodium acetate, or semicarbazide hydrochloride). The main receiver was then filled with these reagents while in a few cases they were added beforehand.

(3) *Isolation of Methylglyoxal*.—Methylglyoxal had previously been identified in the distillate qualitatively by its odor and by its reaction with sodium nitroprusside and piperidine. In all, twenty-six experiments were carried out for the qualitative determinations, and these are shown in Table III. In Experiments 1 and 2, *p*-nitrophenylhydrazine, in Experiments 3 to 7, dinitrophenylhydrazine, in Experiments 8 to 14, the nickel salt of hydroxylamine, and in Experiments 15 to 26, semicarbazide, were used as precipitating agent. The rubber was varied widely, and even gel rubber and gutta-percha were included, without essential differences being found.

(a) The precipitate of *p*-nitrophenylosazone from Experiments 1 and 2 was extracted with hot alcohol in a Soxhlet apparatus until the extract and the residue had the same melting point. The product gave a blue solution in methyl alcoholic potassium hydroxide. From pyridine diluted with alcohol, beautiful red needles were obtained, with a melting point of 285° C. (Analysis I). Since, however, they contained a little ash they were reprecipitated from acetone with water (II).

I.	5.030 mg. substance:	9.440 mg. CO ₂ ,	2.078 mg. H ₂ O
II.	5.790 mg. substance:	11.209 mg. CO ₂ ,	2.610 mg. H ₂ O
	2.470 mg. substance:	0.500 cc. N (20°, 760 mm.)	
	C ₁₄ H ₁₄ N ₆ O ₄ .	Calcd.	C 52.63 H 4.09 N 24.56
		Found	52.60 (I), 52.82 (II), 4.73 (I), 5.04 (II), 23.24 (II).

Microanalysis of a synthetic control sample of the osazone also gave no better values, contrary to macroanalysis, which however was not possible in this case. In an analogous experiment with sol rubber, the precipitate with *p*-nitrophenylhydrazine gave, when extracted with boiling water, a yellow solution of acetaldehyde-*p*-nitrophenylhydrazone. From 14.9 grams of sol rubber 1.3 grams of hydrazone was isolated, which corresponds to 0.319 gram of acetaldehyde, or 1.32 per cent of the carbon skeleton. The melting point was 127° C. (mixed sample, 126.5°).

(b) Precipitation as dinitrophenylosazone in Experiment 3 with gel rubber. Detection of acetaldehyde: The dinitrophenylhydrazone of acetaldehyde, which melted after recrystallization from alcohol at 157° C. (the literature records 147°),¹⁹ was extracted with hot 94 per cent alcohol from the osazone precipitate. The yield of acetaldehyde in Experiment 3 was 1.2 per cent of the carbon skeleton, in Experiments 4 to 6 3.64, 2.63, and 2.61, respectively. At the outset there were indications of these considerable quantities of acetaldehyde, the origin of which is still uncertain. In Communication 13, acetic acid up to 2 per cent was detected. In this work the volatile aldehydes, but no acids, were studied. The dinitrosozone of methylglyoxal, after recrystallization from alcoholic pyridine, melted at 312° C. (uncorr.), with spontaneous decomposition. It gave a blue violet solution in alcoholic potassium hydroxide. (See Experimental Part A1.)

Acetaldehyde-dinitrophenylhydrazone, $C_8H_8O_4N_4$

Calcd. C 42.9, H 3.58, N 25.00

Found C 43.2, H 3.56, N 25.17

5.303 mg. substance: 8.397 mg. CO_2 , 1.689 mg. H_2O . 4.385 mg. substance: 0.979 cc. N (23°, 743 mm.).

Methylglyoxaldinitrophenyloxazone, $C_{15}H_{12}O_8N_8$

Calcd. C 41.6 H 2.77, N 25.9

Found C 43.3, 43.4, H 3.17, 3.50, N 23.58

4.631, 6.299 mg. substance: 7.352, 10.040 mg. CO_2 , 1.351, 1.970 mg. H_2O . 4.051 mg. substance: 0.842 cc. N (20°, 740 mm.).

Synthetic control samples likewise gave bad microanalyses and semi-microanalyses, because of the four nitro groups, and only the macroanalyses gave concordant results.

(c) Precipitation as nickel methylglyoxal } See Table III and Experimental Part
(d) Precipitation as disemicarbazone } A4.

Table III shows that the yields of methylglyoxal are best with semicarbazide; that in 7 hours of overozonization only 0.33 per cent of the carbon skeleton appears in the form of methylglyoxal (Experiment 15), but that after 12 hours of overozonization it reaches 1 per cent, which even after 18, 29, and 45 hours of overozonization (Experiments 16, 18, and 19) is not exceeded to any significant extent. With incomplete ozonization (Experiments 7, 10) no methylglyoxal was detected in most cases. On carrying ozonization to the point of stability to bromine (Experiments 5, 9, 11, 12, and 13), only small quantities of methylglyoxal were formed, *i. e.*, in general no precipitate could be obtained with the nickel-hydroxylamine reagent. With semicarbazide such experiments of course were not carried out, and on account of the solubility of the salt, the data on nickel glyoxime (Experiments 8, 9, 11), are in need of correction as above. It may however be assumed, in view of this fact, that the yield of methylglyoxal after ozonization to the point of stability to bromine does not exceed a value of 0.2 per cent of the carbon skeleton, and that frequently it is considerably below this.

It appears to us rather arbitrary, however, to place any special significance on this point, since only after 12 hours of overozonization did a constant methylgly-

oxal value appear. The type of rubber plays an appreciable part. For example, some very old samples (Experiment 15) were ozonized, one of which was no longer in good condition, although it melted in nitrogen. The result was the same as with strictly freshly prepared samples (Experiments 18 and 19). In Experiment 5 the ozonide was cleaved in the presence of potassium ferrocyanide as reducing agent, which has already been recommended by Harries for this purpose. The result was essentially the same, although in this case ozonization was carried out with particular care with 1 per cent ozone, and was continued for 20 days to the point of stability to bromine. The working up of the ozonide with sulfurous acid, which one of the authors (Socias-Viñals) had found to be particularly satisfactory with mesityl oxide ozonide, was also successfully carried out with rubber, after initial difficulties due to a brown color and to resinification. In these experiments (22-26), no methylglyoxal appeared even after overozonization. Distillation was not continued until removal of the methylglyoxal, but the previously dried ozonide was cleaved in water suspension (20-40 cc.), at first cold and then at 80-90°, in a current of sulfur dioxide. Heating at higher temperatures turned the mixture brown and was therefore avoided. The product was then cooled and treated with semicarbazide acetate solution. In no case did a precipitate form. A control experiment showed that sulfuric acid does not disturb the reaction.

With regard to the length of the rubber molecule, the following calculation is of interest. Theoretically, 6.8 grams of rubber are able to yield 7.2 milligrams of methylglyoxal if the chain length corresponds to 1000 isopentene members with one terminal isoprene group. In Experiment 23, 5.7 grams of rubber theoretically could have given 6.03 milligrams, but actually gave only 2 milligrams. With a cleavage liquid from 40 cc. of sulfuric dioxide solution, 0.05 mg. (50 γ per cc.) were obtained. This quantity was detected qualitatively (page 561) by the semicarbazide method.

D. Comparative Experiments with Methylheptenone (Braun and Matthäus)

Four grams of methylheptenone were dissolved in 125 cc. of chloroform and ozonized ice-cold. The ozonized solution was concentrated first with exclusion of moisture on a 35° C. bath and finally at 20° in a vacuum, after which it was subjected to a high vacuum for 2 hours. The oily residue was interspersed with tiny crystals of acetone peroxide. Cleavage was carried out with addition of 20 cc. water on a water bath at 70-80° in a current of nitrogen until no oil remained in the flask. During the cleavage process, two flasks containing an acetic acid solution of semicarbazide were inserted; after the reaction was ended the temperature of the bath was increased to 150° C. until the distillation residue had become bright yellow, and the greater part of the product had distilled over. The semicarbazones of acetone and methylglyoxal precipitated in the receiver, while the semicarbazone of levulinic aldehyde remained in solution. The semicarbazones which had precipitated were first warmed with sodium carbonate solution in order to remove whatever acid components might be present, and then were extracted with boiling methanol to remove the acetone derivatives.

Three samples which were overozonized for 15, 15, and 48 hours, gave 0.84, 0.63, 0.89 per cent of the carbon skeleton in the form of methylglyoxal, and 0.04, 0.037, 0.43 per cent of the carbon skeleton as oxalic acid. The yields of samples 2 and 3 in levulinic acid were 31.8 and 21.7 per cent, and in levulinic aldehyde 1.7 and 2.7 per cent. Sample 4 was carried only to the point of ozone saturation, and gave no methylglyoxal, no oxalic acid, 19 per cent levulinic acid and 18.4 per cent levulinic aldehyde.

TABLE III

No.	Kind of Rubber (Sol or Gel Fraction in Grams)	Ozone Content (Percentage)	Time of Ozonization (Hours)	Precipitating Agent (Grams)	Methylglyoxal (Percentage of the Carbon Skeleton)
1	Gel (frac. 10)	5.7	107	p-Nitrophenyl-	0.38
2	Gel (frac. 10)	6.5	100	osazone	0.49
3	Gel (frac. 10)	4.3	120	{ 0.3356 0.1522 0.1600 0.0624 ...	0.74
4	Sol (frac. 2)	10.0	140		0.144
5	Sol (frac. 2)	5.4	480		0.284
6	Sol (frac. 1)	5.0	26		0.118
7	Sol (frac. 2)	3.7	2.5		...
8	Total rubber	1.6	Until stable to Br	Ni methylglyoxime	...
9	Sol (frac. 2)	5.0	Until stable to Br	qualitative +	...
10	Sol (frac. 2)	7.0	Just before calcd. stability to Br	0.0129	<0.1
11	Redissolved gel rubber	...	Until stable to Br
12	Sol (frac. 3)	11.5	Until stable to Br	0.002	<0.03
13	Sol (frac. 1)	7.0	Until stable to Br
14	Sol (frac. 1)	6.0	Overozonized 10 hrs. beyond stability to Br
15	Sol crepe	3.5	Overozonized 7.25 hrs.	0.0035	0.009
16	Sol (frac. 2) alkali-sol latex	3.5	Overozonized 18 hrs.	Disemicarbazone	0.33
17	Sol (frac. 2) alkali-sol latex	3.5	Overozonized 12 hrs.	0.0507	1.22
18	Sol (frac. 2) fresh crepe	3.4	Overozonized 29 hrs.	0.1690	1.00
19	Sol (frac. 2) crepe	3.0	Overozonized 45 hrs.	0.1600	1.03
20	Sol (frac. 2) crepe	3.0	Overozonized 21 hrs.	0.1598	1.01
21	Gutta-percha (control experiment for No. 20)	...	Overozonized 21 hrs.	0.1377	1.097
22-26	Sol (frac. 2) 3; 5.7; 3; 3	...	Overozonized 21 hrs.	0.1664	1.097
		...	The first ozonized until stable to Br, the others overozonized	0.1430	1.097
	

Of four additional control tests, Nos. 5 and 6 were carried out under the conditions of Experiment 4, while Nos. 7 and 8 involved considerable overozonization, and in each case the first experiment was carried out without sulfuric acid, and the cleavage of the others was like that of rubber. Only Experiment 7 gave any methylglyoxal. Aside from the larger quantity of oxalic acid which is found with methylheptenone, the analogy to rubber is very close.

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- ³ Pummerer, Ebermayer, and Gerlach, *Ber.*, **64**, 814 (1931).
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- ⁶ For the calculation see Section C-(3)-(d).
- ⁷ We prefer to offer this hypothesis concerning the alkylidene peroxide and in this way to avoid the somewhat indefinite term "oxozonide;" see Fischer, Düll, and Ertel, Reference 5.
- ⁸ *Ber.*, **57**, 1502 (1924).
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- ¹⁴ Levene and Walti, *Chem. Zentr.*, **1926**, II, 1126; "Beilstein," Vol. **XV**, p. 472.
- ¹⁵ Dakin and West, *J. Biol. Chem.*, **15**, 137; Cameron, *Chem. Zentr.*, **1927**, II, 1245.
- ¹⁶ Dakin and Dudley, *Chem. Zentr.*, **1913**, II, 794; "Beilstein," *loc. cit.*
- ¹⁷ *Monatsh. Chem.*, **53-54**, 1031 (1929), Wegscheider-Festschrift. We have not examined in this work the use of α,β -naphthylenediamine, which was recommended by these same authors (*Ber.*, **63**, 3068 (1930)).
- ¹⁸ This is in agreement with Wolff, *Ann.*, **394**, 41 (1912).
- ¹⁹ *J. Chem. Soc.*, London, **52**, 2955 (1930). Socias-Viñals was able to confirm with a synthetic control sample the melting point of 147° given by Allen. However, our sample with a melting point of 157° gave quite uniform results (see above). Attention has already been called to the differences in the melting points of the nitrohydrazones (see Section A-2). Finally, as judged by this melting point, formaldehyde-dinitrophenylhydrazones with a melting point of 155° might also be present. A mixture of the two is not impossible, though this latter compound contains 3 per cent less carbon and 1.5 per cent more nitrogen. In an experiment with gutta-percha by Socias-Viñals, formaldehyde and acetaldehyde were separated with dimedon, and 1.33 per cent of the carbon skeleton was obtained in the form of acetaldehyde, together with 0.32 per cent in the form of formaldehyde.

Properties of Higher Polymers in Solution. III. The Action of Ultra-Violet Light on Dissolved Rubber

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The action of ultra-violet radiation on rubber has been the object of a long series of investigations. According to van Rossem,¹ rubber is depolymerized under the action of light. Asano² on the other hand thinks that ultra-violet light, is able to bring about either polymerization or depolymerization according to its wave-length. More recently Dogadkin and Pantschenkov³ have carried out experiments in an atmosphere of nitrogen, during the course of which they have found a strong diminution in the viscosity. From this fact they have concluded that light is able to cause depolymerization and micellar degradation.

We have undertaken a study of the action of ultra-violet light on rubber in order to prove whether the double *cis*-linkages of rubber undergo a transposition into *trans*-linkages, for numerous instances are known where light causes these *cis-trans*-transpositions. In the case of rubber, one should obtain, therefore, either a hydrocarbon of the gutta-percha type or, if light causes a sort of *cis-trans*-equilibrium, a hydrocarbon with double *cis*-linkages distributed irregularly.

In our experiments we were extremely careful to exclude oxygen, since some years ago Henri⁴ proved that ultra-violet light activates greatly the oxidation of rubber. On the other hand it is known that oxidation causes a diminution in the length of the chains which modifies considerably the physical properties, for example, the viscosity, and which may mask the effect produced by light.

We exposed a dilute cyclohexane solution of slightly masticated rubber to light for a long time. The solution was transformed into an elastic jelly which could not be redissolved by the addition of cyclohexane or by any other solvents. This jelly behaved almost like the product obtained by the reaction of small proportions of sulfur chloride with dilute solutions of rubber.

The jelly obtained by exposure to light resembled closely enough gel rubber⁵ which is present in natural rubber to be mistaken for it. On the other hand it was distinguished from gel rubber by its behavior toward solvents, because gel rubber is readily soluble in toluene containing a little butyl alcohol.

If the two gels show a limited imbibition, the cause must be sought in different phenomena of these two substances. We believe that gel rubber is composed of long chains with points of oxidation. In an apolar solvent these polar points join one another, just as do the carboxyl groups of higher fatty acids in apolar solvents. A loosely constructed tri-dimensional network results by the introduction of these linkages between the dipoles (hydroxyl-bond) of Bernal.⁶ These linkages can be broken by the addition of hydroxylated molecules. Linkages are then established between the oxygenated points of rubber and the hydroxyls of the solvent.

Moreover, the behavior of our product makes inevitable the conclusion that in this jelly the original chains are found grouped in a tri-dimensional network, through the formation of transverse chemical linkages between the chains. Light causes a form of vulcanization by means of irregular polymerization. We assume that these transverse linkages enter between the original double bonds. We have not been able to prove any indication of a *cis-trans*-transposition. On the contrary, the dried jelly, which has the mechanical properties of slightly vulcanized rubber, gives unmistakably, when stretched, the interferences of the original rubber. The result is not even a partial transposition of the double bonds, since in this case irregularities in the network would have been observed.

In another experiment, during which oxygen was not vigorously excluded, we observed a great diminution in the viscosity. After long exposure to light we obtained by evaporation of the cyclohexane a sticky viscous product, which had no longer any characteristic of rubber. This product contained approximately seven per cent of oxygen. When spread out on glass and exposed to air for some time, the product became covered with a solid film which was insoluble in all solvent. This phenomenon is strictly comparable to the drying of linseed oil.

The results of our experiments make it very probable, in our opinion, that the diminution in the viscosity observed by Dogadkin and Pantschenkov after a short exposure can be ascribed to a degradation due to the presence of traces of oxygen.

Experimental Part

As raw material we used a rubber which van Rossem was kind enough to send us. This rubber had been obtained by coagulation of latex which had been washed and centrifuged three times. The rubber had also been masticated. Analysis gave a percentage composition corresponding to C_5H_8 . In a solution of cyclohexane at a concentration of one gram per 100 cubic centimeters, the relative viscosity of this rubber was $\eta_{rel} = 6.3$; and at a concentration of 2.5 grams per 100 cubic centimeters $\eta_{rel} = 51.3$ ($20^\circ C$).

In order to characterize the products with very high molecular weight by means of the viscosity, we consider the true viscosity as a better index than is the relative viscosity. This true viscosity was introduced by Fikentscher, and has been used for example by the I. G. Farbenindustrie A.-G. in order to characterize cellulose derivatives and polymerization products.⁷ As a matter of fact, the relative viscosity varies somewhat as a function of the concentration, whereas the true viscosity is from this point of view a constant. This true viscosity is derived from the empirical equation:

$$\log z = \left(\frac{75 k^2}{1 + 1.5kC} + k \right) C$$

where z is the relative viscosity, C the concentration in grams per 100 cubic centimeters of solution, and k is the true viscosity.

In general the true viscosity is multiplied by 1000, *i. e.*, it is represented by the value $k \times 10^3$. For our product there results from the two values shown for η_{rel} a value of $k \times 10^3 = 103$.

The solvent cyclohexane was freed of all traces of benzene by agitation with a sulfonitric mixture, washed carefully with water, and distilled in a current of nitrogen free of oxygen. After distillation, the solvent was stored with rigorous exclusion of air, and the rubber solution was prepared in an atmosphere of nitrogen.

As a laboratory receptacle we used a 220-cc. quartz Erlenmeyer flask, closed with a cork having three holes, in two of which was an internal cooling system formed of a

glass spiral through which a current of cold water passed. The third opening carried a tube which ended in a U-tube, filled with water. Into the exterior branch of the U-tube a constant stream of nitrogen was bubbled.

This arrangement made it possible for the volume of the contents of the flask to change with changes in temperature. The cork was freed from air by leaving it in liquid paraffin in a vacuum until removal of the gas was complete. Finally it was dipped in collodion.

For the experiments the receptacle was completely filled with a 5 per cent solution in an atmosphere of nitrogen, and exposed continuously for 10 days at 5 cm. distance to the radiation of a 300-watt mercury quartz lamp. After this lapse of time the original viscous liquid was transformed into a homogeneous jelly, which was insoluble in all solvents or mixtures of solvents. On the other hand, this jelly liquified after standing for several days in chloroform in light. We consider this transformation the result of a secondary degradation.

This jelly was freed from the solvent by evaporation, and the product obtained had every appearance of the original product. When stretched and examined by x-rays it showed interferences, and the diagram obtained was likewise identical to the original diagram.

Two experiments with solutions containing 5 grams per 100 cc., in which oxygen was not rigorously eliminated, gave a very different result, i. e., the viscosity diminished very rapidly. At the end of the experiment the relative viscosity of a cyclohexane solution containing 2.5 grams per 100 cc. was no more than 1.46, corresponding to a true viscosity of $k \times 10^3 = 25$. By evaporation, a sticky paste was obtained, analysis of which gave 81.9 per cent of carbon and 11 per cent of hydrogen. It therefore contained 7.1 per cent of oxygen. When exposed to air it became covered with a solid, insoluble skin after a few days.

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Isoprene and Rubber

Part 44.¹ Viscosity Measurements of Squalene and Hydrosqualene Solutions

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The physical properties of highly polymerized substances, which are composed of fiber molecules, depend on the lengths of the chains of these fiber molecules. Thus tensile strength, elasticity, tendency to swell in solvents, and above all viscosity, are dependent on the length of chain of the particular substance. Among the substances, the properties of which vary thus, are rubber, gutta-percha, and balata. Since the length of fiber molecules can vary within wide limits, such physical properties as those mentioned above show wide variations in the case of rubber, gutta-percha, and balata. This is evident for example by a comparison of the properties of unmasticated rubber, which consists of long fiber molecules of a degree of polymerization of 2000, with the properties of masticated rubber, the greatly dissociated molecules of which have a degree of polymerization of only 500.² The determination of the length of the fiber molecules is therefore of great importance in the case of highly polymerized substances. It has already been proved in past experiments with members of a series of homologous polymers, *i. e.*, of substances the macromolecules of which have the same basic structure and differ only in length, that the molecular weights can be determined from viscosity measurements. This determination is based on the fact that there is a general relation between the specific viscosity and the length of the dissolved molecules, which can be expressed by the formula:³

$$\frac{\eta_{sp}}{C_{bm}} = K_m \cdot M \quad (1)$$

where η_{sp}/C_{bm} is the viscosity of a base molar solution, *i. e.*, a solution which contains 68 grams of rubber per liter of solution. This value is obtained by viscosity measurements of solutions of very low viscosities. Since in the case of highly polymerized substances, such as rubber, more is known about degrees of polymerization P than about molecular weights, equation (1) can be rewritten in the following form:

$$\frac{\eta_{sp}}{C_{bm}} = K_p \cdot P \quad (2)$$

where K_p is a new constant, which is derived by multiplying the K_m constant by 68 (the base molar weight). The relations between the viscosity of dilute solutions and the length of chain can also be expressed by the following formula:⁴

$$\eta_{sp} (1.4\%) = y \cdot n \quad (3)$$

where $\eta_{sp} (1.4\%)$ is the viscosity of a solution which contains 1.4 gram of dissolved substance per liter of solution; y is the specific viscosity of a chain member, and n is the number of chain members. The degree of polymerization is obtained by dividing the number of chain members n by 4, while the molecular weight of the rubber is obtained by multiplying this n value by 17.⁵

If it is desired to determine the molecular weight by means of Equation (1), the degree of polymerization by Equation (2), and the number of chain members by Equation (3), the constants K_m , K_p , and y naturally must be known. As has already been shown in earlier investigations,⁶ these constants can, in the case of semicolloidal, *i. e.*, highly degraded, rubbers be determined by comparison of the viscosities of very dilute solutions with the molecular weights determined cryoscopically.

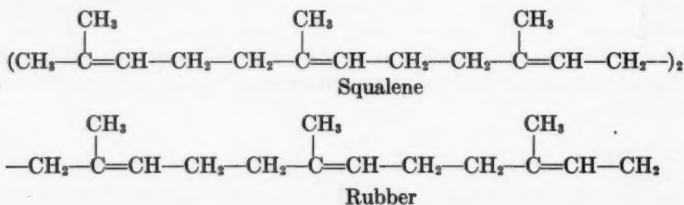
Degraded rubbers are mixtures of homologous polymers, and since they are soft sticky substances and therefore have troublesome physical properties, relatively simple products are difficult to isolate from them. The K_m constants derived from these products are consequently not very precise; they have given a value of 3.0×10^{-4} . A further determination of the K_m constant of semicolloidal balata⁷ gave a value of 3.3×10^{-4} .

The viscosity relations mentioned above were confirmed with substances of low molecular weights, and the y constant was also determined in this case. It was found that this y constant is not exactly the same for all solvents, *e. g.*, in carbon tetrachloride it is approximately 20 per cent higher than in benzene. According to Equation (3) the y value is 1.3×10^{-3} in benzene solutions, and 1.5×10^{-3} in carbon tetrachloride solutions.⁸ These differences are attributable to the fact that the solvents solvate the dissolved substances to different extents.

These investigations of the viscosities of solutions of substances of low molecular weights gave in the case of rubber a calculated K_m constant of 3.7×10^{-4} ; higher therefore than the experimental value. Such differences in constants are of no fundamental significance in calculating in a proximate way the lengths of chain and the degrees of polymerization of rubbers from viscosity measurements. However, for more extensive investigations of the form and length of macromolecules of rubber they should be known more precisely.

Measurements of the Viscosities of Solutions of Squalene⁹

In order to establish more exactly the constants necessary for determining the molecular weight of rubber, viscosity measurements were made of a simple polyene, of low molecular weight, which has the same structure as that of rubber, *viz.*, squalene $C_{30}H_{50}$, the formula¹⁰ of which is shown below in comparison with hexameric isoprene:



Squalene boils at 217°C . under a pressure of 0.01 mm.¹¹ The viscosity measurements¹² were carried out at 20°C . in carbon tetrachloride, benzene, and cyclohexane¹³ in an Ostwald viscometer. The measurements were made at several concentrations. Here too the specific viscosity increased, as in other experiments¹⁴ with dilute solutions, in proportion to the concentration. The η_{sp} (1.4%) values, which were calculated from the viscosity measurements at various concentrations, were constant within the limits of experimental error.

From the viscosity measurements, the y values were calculated by means of

Equation (3), and the K_m constant was calculated by means of Equation (1) (see Table I).

TABLE I. VISCOSITY MEASUREMENTS OF SQUALENE IN DIFFERENT SOLVENTS AT 20° C., $n = 24$

Solvent	Percentage Concentration	C_{bm}	η_r^{15}	η_{sp} (1.4%)	C_{bm}	$\eta \times 10^3$	$K_m \times 10^4$
C_6H_6	5.6	0.823	1.1267	0.0317	0.154	1.32	3.75
	4.2	0.618	1.0960	0.0320	0.155	1.34	3.78
	2.8	0.412	1.0641	0.0320	0.155	1.34	3.78
C_6H_{12}	5.6	0.823	1.1266	0.0317	0.154	1.31	3.75
	4.2	0.618	1.0962	0.0321	0.156	1.34	3.80
	2.8	0.412	1.0634	0.0317	0.154	1.32	3.75
	2.8	0.412	1.0650	0.0325	0.158	1.35	3.85
CCl_4	5.6	0.823	1.1597	0.0399	0.194	1.66	4.73
	4.2	0.618	1.1220	0.0407	0.197	1.70	4.80
	2.8	0.412	1.0776	0.0388	0.189	1.62	4.61
	2.8	0.412	1.0802	0.0401	0.195	1.67	4.75
CCl_4^{18}	5.6	0.823	1.1608	0.0402	0.195	1.68	4.75
	4.2	0.618	1.1223	0.0408	0.198	1.70	4.82

According to measurements shown in Table I, the specific viscosities of solutions of squalene in benzene and in cyclohexane of the same concentration are approximately the same. A η value of 1.3×10^{-3} was obtained, which is the same as that obtained in the case of unbranched hydrocarbons.¹⁷ According to this, benzene solutions of squalene have the same viscosities as solutions of the same concentration of a normal hydrocarbon with the same number of chain members, *i. e.*, $C_{24}H_{50}$. In carbon tetrachloride the η value is 1.68×10^{-3} , while it is 1.5×10^{-3} for the normal paraffin hydrocarbon with unbranched chains. It is therefore 12 per cent higher. Measurements of another sample of squalene gave the same result (see Table I).¹⁸

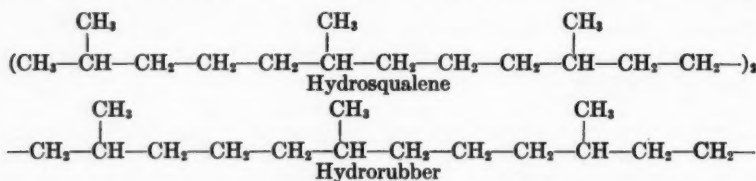
The reason for this difference is not yet obvious. Possibly branched paraffin hydrocarbons are solvated differently from unbranched hydrocarbons; in other words, the solvation of the CH_2 groups in normal hydrocarbons differs from that of the CH_3 groups in squalene.

Viscosity Measurements of Hydrosqualene Solutions

Cryoscopic molecular weight determinations of semicolloidal hydorrubbers and viscosity measurements of their solutions led to a determination of the K_m constants for the hydrocarbons, and thus to the surprising result that this constant is the same for these hydorrubbers and for semicolloidal rubbers, *viz.*, 3×10^{-4} .

According to this, solutions of hydorrubber have the same specific viscosity as solutions of the same concentration of rubber of the same degree of polymerization. This result was surprising, since it was supposed that the solvation of saturated and unsaturated hydrocarbons must differ greatly, and that this difference would be manifest in turn in considerable differences in viscosity. The agreement of the constants shows that differences in solvation of unsaturated and saturated hydrocarbons are insignificant. The specific viscosities of solutions are governed by the lengths of the molecules, but are not influenced in any essential way by double bonds, although the latter do alter considerably many physical properties and above all the chemical properties.¹⁹ This same fact has been found to be true of other simpler compounds of low molecular weights.²⁰

To measure the viscosities of simple hydrocarbons structurally analogous to hydorrubbers, the viscosity of hydrosqualene, $C_{30}H_{62}$, was first of all undertaken.



Hydrosqualene, a hydrocarbon which boils at 195°C . (under 0.01 mm. pressure) was prepared by catalytic reduction of squalene with nickel catalyst, in a Fierz rotary autoclave,²¹ with hydrogen under a pressure of 100.²² The viscosity measurements of this hydrocarbon were carried out in benzene, carbon tetrachloride, and cyclohexane (see Table II).

In benzene and in carbon tetrachloride, the specific viscosity of hydrosqualene is the same as that of squalene. In benzene, the η value is 1.3×10^{-3} , i. e., the same as that of normal paraffin hydrocarbons; in carbon tetrachloride it is approximately 12 per cent higher. Though in the two solvents mentioned the specific viscosity is the same as that of squalene, this is not true of cyclohexane solutions. In this case hydrosqualene is essentially more viscous than squalene, in spite of its having the same length of chain. The η value is 1.7×10^{-3} , whereas it is only 1.3×10^{-3} for squalene. The higher viscosity of hydrosqualene in cyclohexane shows that this saturated hydrocarbon is more strongly solvated by the likewise saturated cyclohexane than is the unsaturated hydrocarbon. It has been found to be true in several other cases of saturated and unsaturated highly polymerized substances²³ that cyclohexane dissolves, and therefore solvates, a saturated hydrocarbon more easily than it does an unsaturated hydrocarbon. This strong solvation results in more highly viscous solutions, as has already been proved in the case of polystyrene.²³

TABLE II.—VISCOSITY MEASUREMENTS OF HYDROSQUALENE IN DIFFERENT SOLVENTS AT 20°C ., $n = 24$

Solvent	Percentage Concentration C_{bm}		η_{sp} ¹⁵	(η_{sp} 1.4%)	$\frac{\eta_{sp}}{C_{bm}}$	$\eta \times 10^3$	$K_m \times 10^4$
C_6H_6	5.6	0.80	1.1236	0.0309	0.154	1.29	3.65
	4.2	0.60	1.0924	0.0308	0.154	1.28	3.65
	2.8	0.40	1.0577	0.0289	0.144	1.21	3.41
C_6H_{12}	5.6	0.80	1.1633	0.0408	0.204	1.70	4.83
	4.2	0.60	1.1167	0.0389	0.194	1.62	4.60
	2.8	0.40	1.0761	0.0381	0.190	1.59	4.50
	2.8	0.40	1.0803	0.0402	0.201	1.67	4.76
CCl_4	5.6	0.80	1.1538	0.0385	0.192	1.60	4.55
	2.8	0.40	1.0760	0.0380	0.190	1.58	4.50
	2.8	0.40	1.0788	0.0394	0.197	1.64	4.67

Comparison of the Constants of Various Polypranes and Polyprenes

In Tables III and IV the various constants of semicolloidal rubbers and hydorrubbers (polyprenes and polypranes) are assembled and compared with the constants of squalene, hydrosqualene, and normal and branched hydrocarbons.

TABLE III.—SUMMARY OF EXPERIMENTALLY FOUND CONSTANTS OF POLYPRENE AND POLYPRANE IN DIFFERENT SOLVENTS

Substance	Solvent	$K_m \times 10^4$	$K_p \times 10^3$	$K_{equiv.} \times 10^4$	$\eta \times 10^3$
Semicolloidal rubber	Benzene	3.0	20	0.75	1.05
Semicolloidal balata	Tetralin	3.3	22.5	0.81	1.15
Semicolloidal hydro-rubber	Benzene	3.0	20	0.75	1.05
Squalene	Benzene	3.77	25.6	0.94	1.33
	Cyclohexane	3.79	25.8	0.94	1.33
	CCl_4	4.74	27.6	1.19	1.67
Hydrosqualene	Benzene	3.57	25.0	0.89	1.26
	Cyclohexane	4.67	32.7	1.17	1.65
	CCl_4	4.57	32.0	1.14	1.64

For comparison the experimentally determined η values and $K_{equiv.}$ constants of normal paraffins are assembled in Table IV, together with the K_m and K_p constants of rubber calculated from them.

TABLE IV

Substance	Solvent	$K_m \times 10^4$	$K_p \times 10^3$	$K_{equiv.} \times 10^4$	$\eta \times 10^3$
Paraffin, etc.	Benzene	3.72	25.3	0.93	1.3
Paraffin, etc.	CCl_4	4.28	29.1	1.07	1.5

Considering that the determination of the constants of semicolloidal rubbers and hydorrubbers is difficult because of troublesome properties, the agreement of these constants with those of squalene, which means with those of simple polymers, is satisfactory. Accordingly the same relations between specific viscosity and chain length hold true of degraded rubbers and hydorrubbers in very dilute solutions as hold true of simple substances of low molecular weights. It is thus evident that molecules of rubber and hydorrubber have the same structure and form as those of squalene and hydrosqualene. Consequently elongated fiber molecules are present in solutions of rubber and hydorrubber. The viscosity law is therefore valid over a wide range in the polyprane and polyprene series, in fact from simple hydrocarbons with a degree of polymerization of 6 to semicolloidal hydrocarbons with a degree of polymerization of about 100.²⁴

Of course it has not yet been proved experimentally that Equations (1), (2), and (3) are applicable to the determination of the molecular weights and degrees of polymerization of rubbers with the highest molecular weights. Nevertheless they probably are valid in this case, as evidenced by investigations of homologous polymeric series of rubbers from the lowest to the highest members.²⁵ Deviations from the Hagen-Poiseuille law, which appear with concentrated solutions of eucolloidal rubbers, are so slight with dilute solutions that they may be disregarded in determining molecular weights.²⁶ Furthermore the validity of the viscosity law up to the highest members of other substances of high molecular weights, particularly cellulose derivatives,²⁷ is already established. Finally it has been shown by means of osmotic measurements of rubber solutions, a subject particularly investigated by Caspari,²⁸ that extremely large molecules are present, in fact with molecular weights of 100,000 and 200,000.

As a consequence, viscosity measurements offer a simple way to determine the molecular weight of rubber, and above all to compare and to distinguish homologous polymeric rubbers of differing degrees of degradation. The constants determined with the aid of squalene for the various solvents are suitable for use provided that the constants for rubber of high molecular weight are not derived from osmotic molecular weight determinations.²⁹

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- ² Staudinger, "Die Hochmolekularen Organischen Verbindungen Kautschuk und Cellulose," Berlin, **1932**.
- ³ Cf. Reference 2, p. 60.
- ⁴ For this conversion of formulas, see Reference 2, p. 69; Staudinger, *Z. Elektrochem.*, **40**, 434 (1934).
- ⁵ For the equivalent weight of chain, see Reference 2, p. 67; Staudinger, *Ber.*, **65**, 267 (1932).
- ⁶ Staudinger, *Kautschuk*, **6**, 153 (1930); Staudinger and Bondy, *Ber.*, **63**, 734 (1930).
- ⁷ See Reference 2, p. 407.
- ⁸ Staudinger, *Z. Elektrochem.*, **40**, 434 (1934); Staudinger and Staiger, *Ber.*, **68**, 707 (1935).
- ⁹ A great number of investigations of squalene have already been carried out by Leupold; cf. Reference 2, pp. 69, 408; Staudinger, *Z. Elektro-Chem.*, **40**, 434 (1934).
- ¹⁰ Karrer, Helfenstein, Wehrli, and Wettstein, *Helv. Chim. Acta*, **13**, 1084 (1930).
- ¹¹ Larger quantities of squalene were placed at our disposal by Professor Heilbron of Liverpool, and we take this occasion to express our great appreciation for this kindness.
- ¹² For the experimental procedure, see Staudinger and Staiger, *Ber.*, **68**, 707 (1935).
- ¹³ Tetralin, in which many viscosity measurements of rubber have been carried out, is not suitable, for the absolute viscosity of tetralin is too high in comparison with that of squalene. The viscosity law can be expected to hold true only when the absolute viscosity of the dissolved substance is very high compared to that of the solvent. See Reference 2, p. 59; Staudinger and Staiger, *Ber.*, **68**, 707 (1935).
- ¹⁴ See Reference 2, p. 56.
- ¹⁵
$$\eta_r = \frac{t_2}{t_1} \cdot \frac{d_2}{d_1}$$
- ¹⁶ Measurements of a second sample.
- ¹⁷ Staudinger and Staiger, *Ber.*, **68**, 707 (1935).
- ¹⁸ Viscosity measurements of carbon tetrachloride solutions of squalene have also been published by Meyer and van der Wyk, *Helv. Chim. Acta*, **18**, 1073 (1935). These investigators found η_{sp} (1.4%) to be 0.0379, from which a calculated η value of 1.58×10^{-3} is obtained.
- ¹⁹ Staudinger and Nodzu, *Helv. Chim. Acta*, **13**, 1350 (1930).
- ²⁰ Staudinger and Ochai, *Z. phys. Chem.*, **158A**, 35 (1932).
- ²¹ Fierz-David, "Farbenchemie," Berlin, **1922**, p. 215.
- ²² Hydrosqualene has already been described by Heilbron (*J. Chem. Soc.*, **1926**, 3131). It has a boiling point at 3 mm. of 224–6° C.
- ²³ Staudinger and Heuer, *Z. phys. Chem.*, **171A**, 129 (1934).
- ²⁴ Staudinger and Leupold, *Helv. Chim. Acta*, **15**, 221 (1932).
- ²⁵ Staudinger and Bondy, *Ann.*, **488**, 153 (1931).
- ²⁶ See Reference 2, p. 210.
- ²⁷ Staudinger and Schulz, *Ber.*, **68**, 2320 (1935); Staudinger and Lohmann, *Ber.*, **68**, 2313 (1935).
- ²⁸ Caspari, *J. Chem. Soc.*, **105**, 2139 (1914); Kroepelin and Brumshagen, *Kolloid-Z.*, **47**, 294 (1929).
- ²⁹ For osmotic molecular weight determinations of substances with high molecular weights, see Staudinger and Schulz, *Ber.*, **68**, 2320, 2336 (1935); *Z. phys. Chem.*, current issue.

Isoprene and Rubber

Part 45. Viscosity Measurements of Solutions of Rubber and Hydorrubber in Various Solvents

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It has been observed many times that solutions of the same concentration of rubber in various solvents show marked differences in viscosity.¹ For example, solutions of rubber in chlorinated solvents such as carbon tetrachloride have higher viscosities than do solutions of the same concentration in benzene or benzine.² These differences in viscosity are attributable to the fact that the rubber molecules are solvated in different ways in the various solvents. It may be further assumed that in a particular homologous series of polymers, all members, *i. e.*, substances of both high and low molecular weights, are solvated in the same solvent in the same way, for only in this way is it possible to believe that the specific viscosity of solutions of like concentration increases with increase in the chain length, as has been found to be true of cellulose derivatives.³

In the previous experiments with squalene and hydrosqualene (cf. preceding article), the constants necessary for calculating molecular weights and chain member indices n were determined. The constants for carbon tetrachloride are higher than those for benzene. In the case of squalene, therefore, as in the case of rubber, carbon tetrachloride gives more viscous solutions than does benzene. If, now, rubbers and hydorrubbers are solvated in the same way as squalene and hydrosqualene, then the same chain lengths of an homologous series of rubber polymers would be obtained by calculations using constants derived from the simple compounds of the chain member index, and from this the degrees of polymerization,⁴ are calculated by means of these constants in the formula:

$$\eta_{sp} (1.4\%) = \gamma n$$

Viscosity Measurements of Masticated Rubber in Various Solvents

For this investigation three samples of rubber degraded by mastication for various lengths of time were studied.⁵ The solvents included not only carbon tetrachloride, cyclohexane, and benzene, but also tetralin and decalin, since these two high boiling solvents are very well adapted to measurements of the viscosities of rubber solutions.⁶ Because of their own high viscosities, the γ values of tetralin and decalin were not determined with squalene and hydrosqualene,⁷ but it is reasonable to assume that the γ value for the polyprenes is the same as that with benzene and cyclohexane, *viz.*, 1.3×10^{-2} .

As the following experiments show, this is indeed the case. Solutions of like concentrations of various homologous rubber polymers in benzene, cyclohexane, tetralin, and decalin have approximately the same viscosities, and only carbon tetrachloride solutions are an exception in that they are more viscous.

By utilizing the γ values derived by means of squalene, approximately the same chain member indices n were obtained from viscosity measurements of the three masticated rubber samples in various solvents. This means that the degrees of

TABLE I. COMPARISON OF THE SPECIFIC VISCOSITIES OF SOLUTIONS OF MASTICATED RUBBER IN VARIOUS SOLVENTS, AND CALCULATIONS OF THE DEGREES OF POLYMERIZATION AND OF THE CHAIN LENGTHS

Rubber No. 1. Masticated 10 min. Average Degree of Polymerization 460

Solvent	$\eta \times 10^3$	% Concentration	η_r	η_{sp} (1.4%)	n	Degree of Polymerization
Carbon tetrachloride	1.70	0.103	1.219	2.89	1750	438
Cyclohexane	1.30	0.108	1.198	2.57	1970	492
Decalin	1.30	0.079	1.144	2.56	1970	492
Tetralin	1.30	0.065	1.108	2.32	1790	448
Benzene	1.30	0.101	1.162	2.24	1720	430

Rubber No. 2. Masticated 20 min. Average Degree of Polymerization 360

Carbon tetrachloride	1.70	0.101	1.159	2.21	1300	325
Cyclohexane	1.30	0.175	1.256	2.05	1580	395
Decalin	1.30	0.110	1.156	1.98	1520	380
Tetralin	1.30	0.096	1.128	1.87	1440	360
Benzene	1.30	0.105	1.139	1.86	1430	358

Rubber No. 3. Masticated 60 min. Average Degree of Polymerization 260

Carbon tetrachloride	1.70	0.221	1.269	1.70	1000	250
Cyclohexane	1.30	0.128	1.129	1.41	1080	270
Decalin	1.30	0.128	1.300	1.42	1090	273
Tetralin	1.30	0.090	1.087	1.35	1040	260
Benzene	1.30	0.106	1.097	1.28	985	246

TABLE II. COMPARISON OF THE SPECIFIC VISCOSITIES OF SOLUTIONS OF SEVERAL HYDRO-RUBBERS IN VARIOUS SOLVENTS, AND CALCULATIONS OF THE DEGREES OF POLYMERIZATION AND OF CHAIN LENGTHS

Hydrorubber No. 1. Average Degree of Polymerization 350

Solvent	$\eta \times 10^3$	% Concentrations	η_r	η_{sp} (1.4%)	n	Degree of Polymerization
Carbon tetrachloride	1.70	0.140	1.212	2.12	1250	313
Cyclohexane	1.70	0.145	1.252	2.44	1430	358
Decalin	1.70	0.095	1.171	2.52	1480	370
Tetralin	1.30	0.124	1.164	1.85	1420	355
Benzene	1.30	0.142	1.123	1.21	930	232

Hydrorubber No. 2. Average Degree of Polymerization 198

Carbon tetrachloride	1.70	0.193	1.173	1.25	735	184
Cyclohexane	1.70	0.177	1.171	1.35	795	199
Decalin	1.70	0.132	1.130	1.37	805	201
Tetralin	1.30	0.214	1.166	1.09	840	210
Benzene	1.30	0.151	1.079	0.73	561	140

Hydrorubber No. 3. Average Degree of Polymerization 158

Carbon tetrachloride	1.70	0.183	1.133	1.02	600	150
Cyclohexane	1.70	0.138	1.103	1.04	610	152
Decalin	1.70	0.142	1.114	1.12	660	165
Tetralin	1.30	0.182	1.111	1.86	660	165
Benzene	1.30	0.125	1.064	1.72	555	139

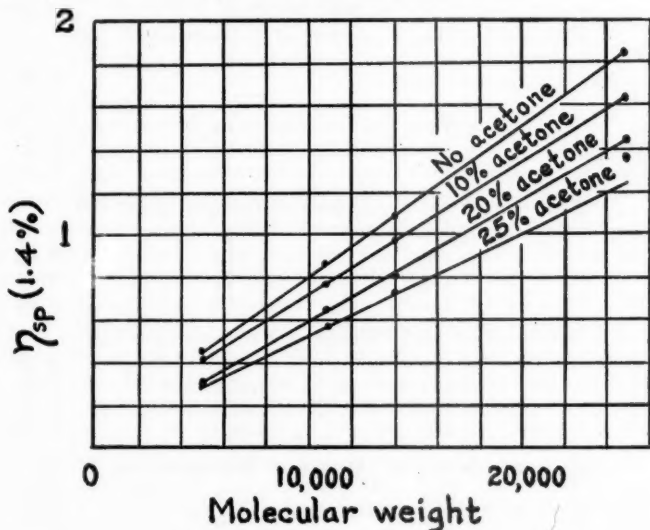
Hydrorubber No. 4. Average Degree of Polymerization 74

Carbon tetrachloride	1.70	0.278	1.094	0.48	282	71
Cyclohexane	1.70	0.225	1.076	0.47	276	69
Decalin	1.70	0.304	1.108	0.49	288	72
Tetralin	1.30	0.098	1.031	0.44	339	85
Benzene	1.30	0.108	1.029	0.38	292	73

polymerization were approximately the same (see Table I). These experiments are to be continued and extended to eucolloidal rubber.

Viscosity Measurements of Homologous Hydrorubber Polymers in Various Solvents

Experiments similar to these with rubber were carried out⁸ with hydrorubbers which had been prepared by catalytic reduction with nickel⁹ at various temperatures. Here too the same solvents were used as for rubber. For calculating the chain member index n in decalin solution the same y value was employed as was employed for cyclohexane, *viz.*, 1.7×10^{-3} , on the assumption that both hydroaromatic hydrocarbons solvate hydrorubber in the same way. For tetralin and benzene, 1.3×10^{-3} was used as constant (see Table II).



In carbon tetrachloride, decalin, and tetralin the four hydrorubbers showed the same degree of polymerization. In benzene, which solvates saturated hydrocarbons relatively little, low values were obtained, indicating that these hydrorubbers are not solvated in benzene to the same extent that hydrosqualene is. This observation again confirms earlier experiments, *viz.*, that it is necessary to use the most powerful solvating agents for determining the chain member index n and the degree of polymerization from viscosity measurements, since only such solvents solvate both high and low molecular members of a series to approximately the same extent. Poor solvents on the contrary solvate the higher members of a series to a less extent than they do the lower molecular members, so that the viscosities of solutions of like concentration of high molecular members are relatively too low. This has already been found experimentally to be true of polystyrene.¹⁰

Viscosity Measurements of Hydrorubber in Mixtures of Solvents and Precipitants

The greater the extent to which fiber molecules are solvated, the higher are the viscosities of solutions of like concentration of substances composed of these

fiber molecules; in other words, the viscosities are higher in good solvents than in poor solvents. Solvents which do not dissolve rubber and hydorrubber, and accordingly solvents by means of which rubber and hydorrubber can be precipitated from their solutions, solvate rubber so little that the molecules cannot pass into solution.

If rubber or hydorrubber is dissolved in such mixtures of good solvents and precipitating agents, the specific viscosities of solutions of the same concentration diminish with increasing proportion of the precipitating liquid. We studied the specific viscosities of hydorrubber at equal concentration in tetralin and in mixtures of tetralin containing increasing proportions of acetone¹¹ (see Table III).

TABLE III. EFFECT OF THE ADDITION OF PRECIPITATING AGENTS ON THE VISCOSITY OF SOLUTIONS OF HYDRORUBBERS IN TETRALIN

Hydorrubber No. 1. Degree of Polymerization 350

% Acetone	% Concentration	η_r	η_{sp} (1.4%)
0	0.124	1.164	1.85
10	0.140	1.163	1.63
20	0.170	1.174	1.43
25	0.141	1.142	1.40

Hydorrubber No. 2. Degree of Polymerization 198

0	0.214	1.166	1.09
10	0.110	1.079	1.00
20	0.129	1.071	0.77
25	0.113	1.058	0.72

Hydorrubber No. 3. Degree of Polymerization 158

0	0.182	1.111	0.86
10	0.139	1.071	0.72
20	0.204	1.098	0.67
25	0.156	1.062	0.56

Hydorrubber No. 4. Degree of Polymerization 74

0	0.098	1.031	0.44
10	0.286	1.083	0.41
20	0.170	1.052	0.43
25	0.360	1.077	0.30

The influence of increasing proportions of acetone on the specific viscosity of hydorrubber solutions is shown graphically in the accompanying illustration.

These experiments confirm the earlier experiments with polystyrenes, for in that case too it was shown repeatedly that the specific viscosities of solutions of polystyrene solutions of like concentration diminish greatly with addition of precipitating agents.¹²

Determination of the Solubility of Hydorrubber in Various Solvents

The lower the solubility of a polystyrene in various solvents, *i. e.*, the less the liquids solvate the polystyrene molecules, the lower the specific viscosities of solution of like concentration in the various solvents.

The solubilities of these high molecular substances can be determined directly only with difficulty, but the solubility can be estimated by determining the proportion of precipitant which must be added to dilute solutions in various solvents in order to start precipitation of the polystyrene. The beginning of this precipitation can be recognized by the appearance of turbidity provided that the index of re-

TABLE IV. PRECIPITATION OF HOMOLOGOUS POLYMERIC HYDRORUBBERS FROM VARIOUS SOLVENTS

(In the Table, the number of cc. of precipitating agent to bring about turbidity in 100 cc. of approximately 0.5 per cent solution is given.)

Solvent	Degree of Polymerization 350			Degree of Polymerization 198		
	Methanol	Acetone	Dioxan	Methanol	Acetone	Dioxan
Cyclohexane	...	51.8	126	...	53	132
Decalin	...	45	105	...	47	113
Tetralin	...	38	95	...	38	91
Benzene	3.2	7.5	9.2	5.5	9.2	15

Solvent	Degree of Polymerization 158			Degree of Polymerization 74		
	Methanol	Acetone	Dioxan	Methanol	Acetone	Dioxan
Cyclohexane	...	53	132	...	55.8	150
Decalin	...	48	114	...	51	129
Tetralin	...	38	91	...	44	98
Benzene	5.3	9.9	15	9.5	10	22.5

fraction of the precipitated substance is sufficiently different from that of the solution. In the case of hydrorubber, the beginning of turbidity cannot be distinguished so sharply as it can be in the case of polystyrenes; nevertheless these methods can be used to determine the solubility of hydrorubber in various solvents.

As solvents we used cyclohexane, decalin, tetralin, and benzene, and as precipitating agents, methanol, acetone, and dioxan. In each case the precipitating agent was added to 100 cc. of approximately 0.5 per cent solutions of various hydrorubbers until turbidity appeared. The greater the volume of precipitating agent necessary to cause precipitation, *i. e.*, turbidity, the better are the dissolved molecules solvated by the solvent. The experiments on the four hydrorubbers (see Table IV) show that the greatest proportion of precipitant must be added to cyclohexane solutions, followed by decalin and tetralin solutions. Relatively little precipitant is sufficient to precipitate hydrorubber from its benzene solutions. This is accordingly further evidence that, in contrast to the first three wholly or partially hydroaromatic solvents, benzene has very little solvating action on hydrorubbers. It is evident then that the same relation found true of polystyrenes holds true in this case also, *viz.*, that a solvent which has little solvent power and therefore little solvating action on a substance gives solutions with low viscosities.

A comparison of the various precipitating agents also shows differences. Hydrorubber is precipitated more readily by acetone than by dioxan, indicating in turn that acetone solvates hydrorubber still less than does dioxan. Methyl alcohol can be used as a precipitating agent only with benzene, since it is only slightly soluble in cyclohexane, decalin, and tetralin. Methyl alcohol is nevertheless the best precipitant for hydrorubbers, and very small proportions are sufficient for precipitation. The solubility of hydrorubber in methanol is therefore extremely slight.

Finally if the solubilities of the various homologous polymeric hydrorubbers are compared on a basis of the precipitation experiments, it is found that the solubilities are not the same but diminish with increase in the degree of polymerization. These differences in solubility are particularly evident in the precipitation of benzene solutions of various homologous hydrorubber polymers by means of methyl alcohol. Larger proportions of methanol are necessary for the low polymers than for the high polymers. The solubilities and the states of solvation of the low polymers are therefore greater than those of the higher polymers.

These differences in solubility are much less pronounced in good solvents, such

as cyclohexane and decalin, than in poor solvents, such as benzene. In good solvents, therefore, the members of an homologous series of polymers are solvated to approximately the same extent. This confirms the earlier experiments, *viz.*, that in order to determine the chain lengths of fibre molecules by means of viscosity measurements, it is necessary to carry out the latter with good solvents. The precipitation method offers a simple means of distinguishing whether a solvent has a good or a poor solvating action on a particular highly polymerized substance, and, consequently, it gives an opportunity to choose the correct solvent for determining chain lengths by means of viscosity measurements.

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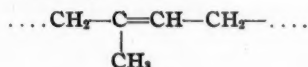
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- ² Kirchhof, *Kolloid-Z.*, **1914**, 30.
- ³ Staudinger and Schulz, *Ber.*, **68**, 2320 (1935).
- ⁴ The tables which follow include only the chain lengths and degrees of polymerization, since these are essential in connection with the physical properties of high polymers.
- ⁵ These samples were furnished by the I. G. Farbenindustrie A.-G., Ludwigshafen, to whom our sincere thanks are due.
- ⁶ Staudinger, "Die Hochmolekularen Organischen Verbindungen Kautschuk und Cellulose," Berlin, **1932**, 417.
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The Diffraction of Electrons by Rubber

J. J. Trillat and H. Motz

One of us has shown that it is possible to obtain diagrams of electronic diffraction with thin films of organic substances, such as fat acids and paraffins,¹ cellulose and its derivatives.²

The substances studied until now have not been selected at random; they belong to the fundamental types of linear carbon chains which are formed by repetition in one direction of identical elements ($-\text{CH}_2$ or glucoside residues). It was likewise important to study chains of the type of which rubber is constituted, and which are formed by repetition of the isoprene residue:



We endeavored to determine whether electronic analysis, with its potentially great field of investigation, could not be utilized successfully in this case. With this end in view we prepared, by means of a technic which will be described in another article, rubber films several $\mu\mu$ in thickness (of either smoked sheet or crepe). These films were stretched about 100 per cent, and were examined by impinging in a direction perpendicular to their surface a pencil of monokinetic electrons, which were accelerated by a difference in potential of 30,000-40,000 volts.

Under these conditions there were visible on the fluorescent screen two types of diffraction patterns: (1) three "amorphous" halos, when the preparation was too thick or had not been stretched, and (2) very small points regularly distributed (see diagram).

A detailed study of these phenomena leads to the following conclusions.

In the first place the point diagrams appear distinct only in the case of elongated samples (approximately 100 per cent elongation). The incidental electrons are therefore diffracted by molecular groups which are regularly arranged and oriented, acting like a single crystal. This confirms the result already known (Katz, Mark, Meyer, and Rosbaud) that stretched rubber is birefringent, and that with x-rays crystalline interferences appear when the degree of elongation is at least 100 per cent. However, these latter interferences are sharp only at elongations of 500 to 700 per cent, whereas electronic analysis shows that crystallization actually takes place in the case of thin films at much lower elongations.

In addition to this, the investigation has shown that pseudo-crystallization is not stable. It can be obtained only with films which are freshly prepared and are examined immediately after being elongated. The diffraction points disappear progressively with time (in about 24 hours), and still more rapidly under the action of incidental electrons (thermal effect).

In any case, it has been proved that crystalline regions do not pre-exist in an unstretched film, for it would not be possible for them to escape detection by electronic analysis. In other words, rubber at rest is made up of chains of isoprene arranged at random and coiled on one another, *i. e.*, with an amorphous structure giving diagrams of the first type. Tension orients these chains by arranging them in parallel

formation, according to a periodic distribution, thus forming a true artificial crystalline structure. This is not the case with films of acetylcellulose or nitrocellulose, which crystallize perfectly without tension under the influence of internal stresses alone,² whereas in the case of rubber it is necessary for a supplementary directing force to intervene.

It is probable that this difference is due to the fact that the principal valence chains constituting cellulose and its derivatives are rigid, whereas those of rubber are deformable, *i. e.*, are coiled on themselves, and assume a regular arrangement only when they unfold as a result of stretching. This deformability, which is attributable to the presence of a double bond, is the cause of the elasticity of rubber.

The electronic diagrams of rubber furnish a number of spots higher than the x-ray diagrams, and furthermore they make possible an exact determination of two sides of the elementary lattice, whereas x-rays give the identity period only along the fibre axis.

To interpret these diagrams, we have indicated these points with their indices on the diagram shown. The surface of the stretched film is made up of a network of rectangular form, the dimensions of which are $c = 8.1$ A. U., $a = 12.4$ A. U. It is of interest to verify that the first of these distances, which corresponds to the fibre axis, is identical with that found by x-rays (Meyer and Mark). The second distance coincides just as precisely with one of the dimensions of the network which these authors have deduced with the aid of

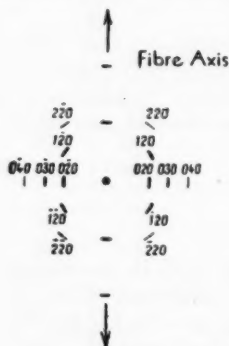
several hypotheses. In our case, however, this result was obtained in a direct way, and thus leads to complete confirmation of the theories of Meyer and Mark. Moreover, the position and the equidistances calculated for most of the points is identical with those obtained by x-rays.

In addition, our experiments show that the isoprene chains are arranged flat on the surface of the film when the film is oriented by tension.

Finally on our photographs there are some points which do not belong to the network of oriented rubber. The cause of the appearance of these points remains to be explained.

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- ² *Compt. rend.*, **198**, 1025 (1934).



The beta-Modification of Gutta-percha Hydrocarbon

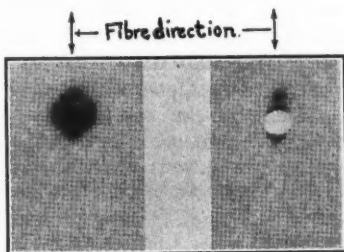
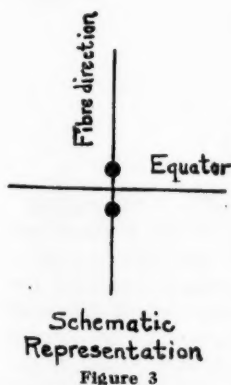
Georg W. Pankow

ZÜRICH, SWITZERLAND

Clark¹ and later Hopff and von Susich² have shown that there are two modifications of gutta-percha hydrocarbon. Hauser and von Susich³ have studied very carefully the transformation of one modification into the other, and have obtained good x-ray fibre diagrams of both. The identity periods in the direction of elongation were 8.8 A. U. for the α -modification and 4.8 A. U. for the β -modification.

The following surprising observation was made: In the fibre diagram of elongated well oriented β -gutta there was found, in addition to the already well known interferences, an interference at a very small angle of deflection in a direction parallel to the fibre axis, corresponding to a lattice plane distance of approximately 115 A. U., *i. e.*, about twenty-four times the identity period.

β -Gutta.—Filtered copper radiation, 30 kv., 16 milliamperes. Distance of film 202 millimeters. Screen 0.3 millimeter in diameter. The deep central blackening in Fig. 1 is due to direct radiation which in the photograph in Fig. 2 is intercepted by a lead plate.



With other screens and with twisting of the fibre axis, the same interference was observed and always in the direction of the fibre axis. It was not evident in the blank photographs. It cannot be a question of total reflection, since the sample completely covered the path of light.

The significance of this observation is not yet definitely settled. The fibre molecules, of which it is believed that gutta-percha is composed, are, according to the present concept, chains of regular successive isoprene residues, C_5H_8 .

In order to explain the appearance of the interferences observed, it must be assumed that these chains form crystallized regions, which in the case of β -gutta show in the fibre direction a well defined second periodicity of approximately 115 A. U. (besides that of 4.8 A. U., shown in Fig. 3).

Meantime it is as difficult to say what distinguishes the chains in the subsequent positions at these distances as it is to define the nature of the end groups.

The observation described here is therefore especially interesting, because an

interference which is related to the length of the molecules has not been known heretofore in the case of natural highly polymerized substances.⁴

It would be desirable to repeat the photographs with long wave x-rays as a control experiment.

The photographs were taken in the Laboratory of Organic and Inorganic Chemistry of the University of Geneva.

References

¹ *Ind. Eng. Chem.*, **18**, 1131 (1926).

² *Kautschuk*, **6**, 234 (1930).

³ *Ibid.*, **7**, 120 (1931).

⁴ *Katz, Trans. Faraday Soc.*, **32**, 80 (1936).

Production of Gasoline by Means of Hydrodepolymerization of Rubber

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Hydrogenation applied to the production of motor fuels from rubber has recently been investigated (C. M. Cowley and J. G. King, *J. Soc. Chem. Ind.*, **54**, 177T (1935)), but this must not be confused with the much more simple hydrogenation process employed in the hardening of fat oils, for a substance of such high molecular weight as rubber may be depolymerized into hydrocarbon oils of much lower molecular weight by hydrogenation, so the process is described more accurately as "hydrodepolymerization." A further important fact concerning the hydrodepolymerization of rubber is that the product probably contains very large amounts of iso-paraffin hydrocarbons. The present authors naturally assume that motor fuels thus obtained are of high knock-rating, since branched-chain paraffin hydrocarbons have much higher knock-ratings than their straight-chain homologs (Lovell, Campbell, and Boyd, *Ind. Eng. Chem.*, **23**, 26 (1931)). The following experimental results prove this assumption correct.

Experimental

The experimental procedure comprised heating pale sheet rubber to be hydrodepolymerized in contact with a catalyst of equal parts of Japanese acid clay and nickel oxide under high pressures of hydrogen in a nickel-chrome-steel autoclave. A transformer oil, whose properties are shown in Table I, was used as solvent.

TABLE I
PROPERTIES OF THE TRANSFORMER OIL USED AS THE SOLVENT OF RUBBER

Specific gravity, d_{4}^{20}	0.9008
Viscosity (Redwood)	
at 20° C.	108"
at 50° C.	46"
at 75° C.	37"
Flash point	147° C.
Cold point	-48° C.
Acid value	0.02

Experiment 1—Thirty grams of rubber dissolved in 300 cc. of transformer oil were charged into an autoclave (having an internal volume of 550 cc. and capable of sustaining 350 atm. at 500° C.) with 15 grams of the mixed catalyst, and hydrogen was admitted to about 30 atm. pressure at the ordinary temperature, the autoclave was heated electrically with shaking, and the change of pressure read by a manometer. The temperature reached 350° C. in 2 hours. After 5 hours at 350° C., the autoclave was cooled to room temperature, and 30 cc. of the product was replaced by 30 grams of rubber. The procedure was then repeated; 30 cc. of the second product was replaced by 30 grams of rubber, and so on. During all of ten experiments thus repeated, the catalyst and transformer oil introduced in the first experiment, were used without further additions. The quantities of hydrogen consumed in each hydrodepolymerization are given in Table II.

TABLE II

QUANTITIES OF HYDROGEN ABSORBED IN THE HYDRODEPOLYMERIZATION OF RUBBER

Reaction	Reaction Temperature, ° C.	Reaction Time, Hrs.	Initial H ₂ -Pressure, Atm.	Maximum H ₂ -Pressure, Atm.	H ₂ Absorbed, Cc. per G.
1	350	5	29.5	56.0	115
2	350	5	30.5	57.0	128
3	350	5	30.0	56.5	115
4	350	5	31.5	58.0	129
5	350	5	29.5	56.5	113
6	350	5	33.0	59.5	109
7	350	5	27.0	53.5	102
8	350	5	27.0	54.0	91.4
9	350	5	28.0	55.0	97.1
10	350	5	28.5	56.0	127
Mean					113

Here, the H₂ absorbed in cc. per g. means the cc. of hydrogen under normal conditions absorbed by 1 gram of rubber. It was calculated from the difference in pressure before and after each experiment, assuming that the transformer oil absorbed no hydrogen.

Table III gives the result of a fractional distillation and the yield of the gasoline fraction produced from rubber by the procedure described above.

Here, the total percentage yield denotes the volume-percentage of the gasoline fraction produced with respect to the total quantities of rubber treated (300 g. or 322 cc.).

TABLE III

FRACTIONAL DISTILLATION OF THE OIL PRODUCED BY HYDRODEPOLYMERIZATION OF RUBBER

I.B.P., ° C.	Hydrodepolym- erized Oil	Autoclave Residual Oil	Total Yield	
			Cc.	%
43	43	43
100° C.	3.1 cc.	4.8 cc.	7.9	2.47
110° C.	4.4 cc.	7.9 cc.	12.3	3.85
120° C.	5.9 cc.	11.0 cc.	16.9	5.29
130° C.	9.3 cc.	13.9 cc.	23.2	7.22
140° C.	10.0 cc.	16.1 cc.	26.1	8.10
150° C.	11.1 cc.	18.0 cc.	29.1	9.05
160° C.	14.9 cc.	21.6 cc.	36.5	11.3
170° C.	25.5 cc.	39.2 cc.	64.7	20.1
180° C.	30.4 cc.	52.0 cc.	82.4	25.6
190° C.	37.4 cc.	54.5 cc.	91.9	28.5
200° C.	45.8 cc.	57.7 cc.	105.5	32.2
210° C.	47.9 cc.	59.9 cc.	107.4	33.4
220° C.	49.0 cc.	66.0 cc.	115.0	35.8

Experiment 2—Thirty grams of rubber dissolved in 300 cc. of transformer oil were introduced into the autoclave with 15 grams of the mixed catalyst, and hydrogen was charged in. The autoclave was heated as before and held at various temperatures from 350° C. to 400° C. for about 10 hours. After each hydrodepolymerization, 30 cc. of the product was replaced by 30 grams of rubber and the same procedure repeated ten times. Table IV shows the quantities of hydrogen absorbed by each hydrodepolymerization thus repeated.

As seen in Tables II and IV, the quantities of hydrogen absorbed by the hydrodepolymerization increase with increase in temperature and duration of the reaction. Table V shows the fractional distillation and the yield of the gasoline thus produced.

A comparison of the results in Table V and those in Table III shows that the yield of the gasoline fraction produced by hydrodepolymerization increases with

TABLE IV
QUANTITIES OF HYDROGEN ABSORBED BY HYDRODEPOLYMERIZATION OF RUBBER

Reaction	Reaction Temperature, ° C.	Reaction Time, Hrs.	Initial H ₂ -Pressure, Atm.	Maximum H ₂ -Pressure, Atm.	H ₂ -Absorbed, Cc. per G.
1	350	10.0	34.5	61.5	168
2	350	12.0	31.0	60.0	142
3	350	10.5	30.0	59.0	173
4	400	10.5	41.5	72.0	263
5	400	10.0	42.0	72.5	259
6	350	11.5	40.0	68.5	167
7	375	8.0	41.0	70.5	237
8	350	10.0	40.5	69.0	191
9	350	10.5	42.0	69.5	170
10	350	12.5	35.5	62.5	168

increase in temperature and duration of the reaction. The yields range from 30 to 60 per cent by volume at reaction temperatures of 350–400° C.

The following table gives the characteristics of the mixed gasoline fractions obtained in Experiments 1 and 2.

Thus, gasolines produced by the hydrodepolymerization of rubber are characterized by their high anti-knock values. In the case of hydro-cracking of heavy

TABLE V
FRACTIONAL DISTILLATION TEST OF THE OIL PRODUCED BY HYDRODEPOLYMERIZATION OF RUBBER

° C. I.B.P., ° C.	Hydrodepoly- merized Oil	Autoclave Residual Oil	Total Yield	
			Cc.	%
44	41
100° C.	11.5 cc.	25.7 cc.	37.2	11.5
110° C.	16.0 cc.	30.2 cc.	46.2	14.3
120° C.	18.1 cc.	34.9 cc.	53.0	16.4
130° C.	23.1 cc.	39.0 cc.	62.1	19.3
140° C.	...	43.5 cc.
150° C.	27.2 cc.	47.9 cc.	75.1	23.3
160° C.	32.4 cc.	56.7 cc.	89.1	27.7
170° C.	43.9 cc.	85.7 cc.	129.6	40.2
180° C.	52.4 cc.	102 cc.	154.4	48.1
190° C.	56.5 cc.	106 cc.	162.5	50.6
200° C.	61.2 cc.	112 cc.	173.2	53.9
210° C.	66.6 cc.	118 cc.	184.6	57.3
220° C.	71.0 cc.	128 cc.	199.0	61.8

petroleum oils, the gasoline produced by low temperature operation, *i. e.*, at 400° C. or below, are of extraordinarily low knock-rating (Haslam, Russell, and Asbury, *Proc. World Petroleum Congress*, London, 1933). It may be naturally concluded that gasolines from the hydrodepolymerization of rubber presumably contain large proportions of branched-chain paraffin hydrocarbons. This is the reason why these gasolines have high knock-ratings.

The present authors are grateful to Prof. Yoshio Tanaka for his helpful advice and to Mr. Kikuo Tozyo for his aid during this work.

TABLE VI
CHARACTERISTICS OF THE GASOLINE FRACTION PRODUCED BY HYDRODEPOLYMERIZATION
OF RUBBER

Specific gravity, d_{4}^{20}	0.8092
Color (Union)	
fresh distillate	2.0
after 48 hours	2.4
after 120 hours	2.8
after 192 hours	3.0
after 264 hours	3.2
Distillation,	
I.B.P.	42° C.
100° C.	14.3%
110° C.	18.6%
120° C.	22.2%
130° C.	27.2%
140° C.	30.0%
150° C.	33.1%
160° C.	39.8%
170° C.	61.9%
180° C.	75.5%
190° C.	81.0%
200° C.	88.2%
210° C.	92.9%
220° C.	97.5%
F.B.P.	227° C.
Copper plate test	Negative
Doctor test	Negative
Silver nitrate test	Negative
Sulfur content (the lamp method)	Trace
Copper dish gum, mg. per 100 cc.	0.5
Blending octane number (motor method)	79.0

The Oil Resistance of Rubber

III. Viscosities and Molecular Polarizations of Rubber Solutions

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The present investigation, deals with the dielectric properties of rubber solutions of several viscosities. Two samples were used: a crude rubber prepared from ammonia-preserved latex by coagulating with acetone and drying in a vacuum desiccator; the other a purified rubber which had been used in previous experi-

TABLE I

Concentration W%	Mol Fraction C_2	Density d_{25}^{25}	Dielectric Constant, $\epsilon_{1.1}$	Refractive Index, n_D^{25}	Molecular Polarization of Rubber, P_2	Electron Polarization of Rubber, PE_2
3.391	0.00501	0.8767	2.2915	1.5008	183.89	176.74
2.605	382	0.8761	2.2905	1.5007	184.06	178.73
1.808	263	0.8756	2.2898	1.5004	184.60	168.95
0.539	078	0.8748	2.2885	1.5001	186.16	174.07

$$\mu = 0.72 \times 10^{-18} \text{ e.s.u.}$$

ments (*J. Soc. Chem. Ind. Japan*, **38**, Suppl. binding, 506 (1935)). The apparatus used to determine dielectric constants, specific gravities and refractive indices and the purifying methods of solvents were the same as in the previous work. The viscosities were measured by an Ostwald viscometer (capillary bore 0.7 mm., length 150 mm.) in a water thermostat at 25° C.

TABLE II

C	2.97	2.28	1.58	0.47
η_{sp}	23.66	17.05	11.82	• 3.50
f	30.4	38.2	52.2	124.1

Experiment A. Molecular Polarization of Crude Rubber. Unmasticated crude rubber could not be dissolved entirely by shaking with benzene. Ostwald asserted that data on unmasticated rubber were too irregular to obtain P_2 from them (*Kolloid*

TABLE III

Number of Times of Puri- fication	P_2	PE	P_0	$\mu \times 10^{-18}$	η_p/C
0	187.0	174.6	12.4	0.72	7.48
1	200.1	176.2	23.9	1.07	5.74
2	200.1	173.3	26.8	1.14	5.16
3	203.6	175.6	28.0	1.16	4.81
4	213.9	178.2	35.7	1.31	4.43
5	227.5	177.4	50.1	1.55	4.22

Z., 70, 75 (1935)). However, the benzene extract of unmastered rubber gives fairly viscous solutions and consistent data were obtained, as shown in the following table.

From these data, the molecular polarization and dipole moment of crude rubber were found to be 187.0 and 0.72×10^{-18} e. s. u., while the moment of purified rubber was about 3×10^{-18} e. s. u., as reported in the previous paper. In this calculation and also in the previous paper, the unit molecule of rubber which moves freely in dilute solution in an electric field was assumed as a group of eight isoprene units. The viscosity data are shown in Table II. f in the table means the specific volume

which is derived from Mark and Fikentscher's equation (*Kolloid Z.*, 49, 135 (1929)), namely, $f = 100\eta_{sp}/C(2.5 + \eta_{sp})$, in which η_{sp} is the specific viscosity and C the concentration (grams of solute in solution of 100 cc.).

The f value is not constant, as shown in the results above. This may be caused by the fact that the viscosities of such thick solutions as in this experiment do not follow Meyer's or Einstein's equation, from which the former is derived.

Experiment B.—Effect of Refining on the Molecular Polarization of Crude Rubber.—As shown in Experiment A, the molecular polarization of crude rubber is far lower than that of purified rubber. The increase of polarity by refining is attributable to the autooxidation of the rubber, which had been deprived of its impurities with antioxidantizing power. To confirm this presumption, the molecular polarization of crude rubber dissolved in benzene and precipitated with ethyl alcohol for various times was observed.

Experiment C.—Effect of Ultra-violet Radiation on Molecular Polarization and Viscosity.—Many investigators have shown that the viscosities of rubber

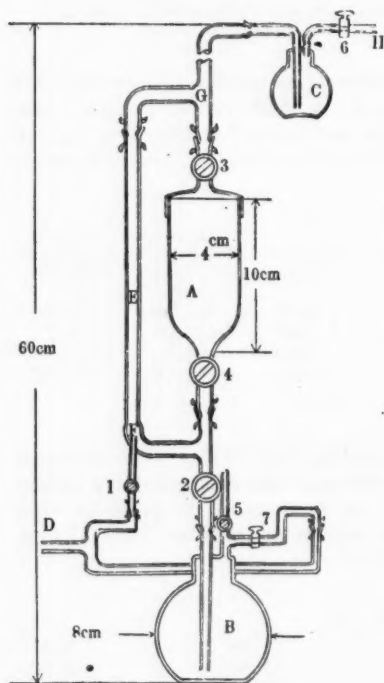


Figure 1

solutions decrease by exposure to ultra-violet radiation. To determine whether this decrease accompanies the reduction of polarity, an experiment on a rubber solution under irradiation was carried out.

Experiment D.—Molecular Polarization of Rubber Purified and Dissolved in an Atmosphere of Nitrogen.—To purify and dissolve rubber in nitrogen, the extractor shown in Fig. 1 was devised. A is a rubber container in which a cylindrical filter paper containing about 3 grams of crude rubber is placed. Acetone in a glass flask B is forced up into A by nitrogen pressure from D, and then circulated by nitrogen bubbles from F. The circulating acetone extracts the rubber in A for 40 hours. The acetone is then restored to flask B, and the sample container A is connected directly to a vacuum pump. After complete drying of the extracted rubber is assured by weighing the container at intervals, the acetone in B is replaced by purified benzene freed from oxygen and its circulation is carried on as well as

acetone. After several hours, the benzene is returned to flask B, and used for measurements of its dielectric properties and viscosity. By manipulating seven cocks shown in Fig. 1, air is completely shut out from the rubber during the refining and dissolving. However, a slight autooxidation while the dielectric constant and viscosity are being measured is unavoidable. The measurements were made on one solution and dilution to obtain $P_{2\infty}$ was not attempted. The results are shown in the following table.

TABLE IV

Time Irradiated (Hrs.)		0	1	2
Crude rubber (in air)	P_2	187.0	191.3	195.2
	η_{sp}/C	7.48	4.92	3.45
Crude rubber (in an atmosphere of nitrogen)	P_2	187.0	188.2	185.7
	η_{sp}/C	7.48	6.28	5.30
Purified rubber (in air)	P_2	302.5	309.3	311.6
	η_{sp}/C	1.56	0.74
Purified rubber (in an atmosphere of nitrogen)	P_2	302.5	303.6	304.2
	η_{sp}/C	1.56	1.21

Time Irradiated (Hrs.)	3	5	10	20	30
Crude rubber (in air)	195.0	198.3	200.8	206.3	215.9
	2.63	1.40	0.27	0.00
Crude rubber (in an atmosphere of nitrogen)	191.6	190.2	191.8	197.3	195.4
	4.50	3.16	1.40	0.18	0.03
Purified rubber (in air)	310.0	312.8	324.0	326.3	327.6
	0.20	0.06	0.03	0.00	0.00
Purified rubber (in an atmosphere of nitrogen)	304.6	305.3	309.3	308.4	307.7
	0.80	0.44	0.01	0.00

TABLE V

	W%	C_2	d^{25}_{15}	Dielectric Constant	η^{25}_D
A	0.649	0.00094	0.8748	2.2885	1.5001
B	0.771	0.00111	0.8749	2.2900	1.5002
	P_2	$P_{B.2}$	$\mu \times 10^{-18}$	η_{sp}/C	
A	186.4	175.8	0.71	4.28	
B	203.4	178.2	1.10	0.12	

A: benzene solution of rubber extracted by acetone in nitrogen for 40 hours.

B: after ultra-violet irradiation in nitrogen for 30 hours on the above rubber solution.

Discussion and Summary

The molecular polarization of crude rubber has no relation to the viscosities of its solutions. For instance, ultra-violet irradiation of crude rubber solutions reduces their viscosities, but does not change essentially their molecular polarizations. With increased refining of crude rubber, its polarization increases, as shown in Experiment B and in the previous work. This may be caused by autooxidation of purified rubber, which contains a lower proportion of impurities which act as natural anti-oxidants. It is probable that by such autooxidation, oxygen combines at the extremity of the rubber molecule, where free isoprene bonds remain. If thread-like molecules of rubber exist, as maintained by Staudinger, a decrease of molecular polarization with reduction of viscosity which results by "cracking" of such long molecules should be observed. Such an effect was not obtained in this experiment. From this point of view, the macro-molecular theory of Staudinger seems to be questionable. The molecular polarization of rubber extracted by acetone for 40 hours and dissolved in benzene in an atmosphere of nitrogen is far smaller than that of purified rubber which has been refined with access of air.

By ultra-violet irradiation in nitrogen of the rubber solution having small polarities, there is no remarkable increase in the polarization of the rubber. From these experiments it is concluded that rubber is a substance having a small polarity, and that it dissolves in benzene in a micellar state or a more complex state having some "structure," but not as thread-like molecules.

Acknowledgment

The author wishes to express his sincere appreciation to Professor Yoshio Tanaka for his valuable suggestions and criticisms.

The Effect of Pigment Particle Size on Some Physical Properties of Rubber Compounds

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The importance of flow in rubber on the reinforcing properties of pigmented systems has been emphasized by Park.¹ He suggests that: (1) in the presence of a finely divided pigment, the flow which occurs when a piece of rubber is stretched takes place in the capillary spaces between the pigment particles; (2) some modification of the laws of liquid flow may govern the behavior of rubber with reference

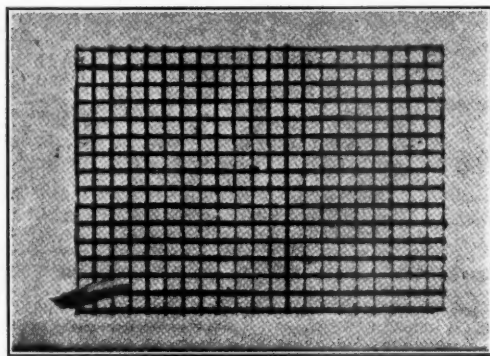


Figure 1—Marking of Vulcanized Squares

to pigments embedded in it, and (3) the forces causing increased stiffness in pigmented rubber compounds are similar to those causing increased resistance to flow of liquids in tubes of capillary dimensions. Thus increasing fineness of subdivision and the resulting fineness of capillary spaces between the particles should be accompanied by an increase in reinforcing properties.

It would be desirable to study the actual stresses around pigment particles in rubber under strain, but so far no suitable microscopic set-up has been devised. A few years ago the writer, resorting to analogies, measured the strains and stresses around large particles with the assumption that the strains would be relatively the same with small particles. For this study, holes of the desired size and shape were cut in strips of calendered but uncured rubber and fitted with pieces of an uncured semihard rubber compound. After vulcanization squares were marked on the tensile sheets as shown in Fig. 1.

With no particles in the sheet the strains remained uniform on elongation, as shown by Fig. 2. However, when particles were inserted, as in Figs. 3 to 7, the stresses became uneven and strains were greater around the particles. These uneven strains caused by the particles resemble very much the lines of flow of a liquid past an object. The percentage elongation was obtained from the photo-

graphs and, with the load known, it was possible to draw the stress-strain curve for any part of the tensile sheet.

In Fig. 8, stress is shown for varying distances from the particle for circular and rectangular particles. When no particle is present, the corresponding stress in the rubber is 125 pounds per square inch, corresponding to 225 per cent elongation and this stress is shown by the horizontal line. All of the curves approach this line as the distance from the particle increases.

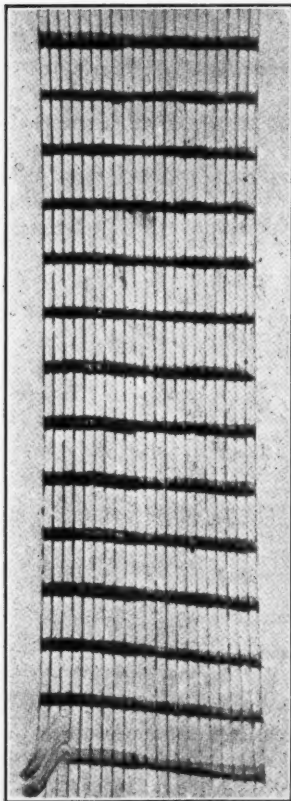


Figure 2—Uniform Strain, No Particles in the Sheet

Two conclusions are possible from Fig. 8.

1. Stresses are greater at the surface of large particles than smaller ones. This agrees with Schippel,² who found that for the same material the volume increase under strain varied directly with the particle size.
2. The stress in the vicinity of a rectangular particle is great if the particle is oriented with its length parallel to the direction of pull, but small if oriented normal to this direction.

The stress-strain curve of unpigmented rubber may be considered as of two parts, one parallel to the strain axis (soft) and the other parallel to the stress axis (stiff). According to Figs. 3 to 8, the addition of pigment causes the strain on considerable of the rubber to be raised to the stiff part of the stress-strain curve when the average rubber would normally be in the soft part of the curve.

The magnitude of this stiffening action may be determined by the size, shape, size distribution, or dispersion of the pigment. Figure 9 shows a series of stress strain curves for circular and rectangular particles. The values for the stress are those found by extrapolating curves similar to those in Fig. 8 to the stress axis. The elongations, as abscissae, are those for the rubber as a whole. Here again the greatest stiffening is obtained with the rectangular particle oriented lengthwise to the direction of extension. In the case of circular particles, the magnitude of the stiffening by the particle depends on its diameter. Between particles of one and two centimeters in diameter, there is an increase in strain of 32 per cent for the section of maximum concentration of stress; between particles of one and three centimeters in diameter, the increase is 48 per cent. These increases are in the ratio of one to one and one-half, which is the same as the ratio of diameters. It has been calculated³ that for an expanded tetrahedral arrangement (which gives a greater interparticulate distance than an expanded cubical arrangement) in a vulcanizate containing 20 volumes of carbon black the particles are distant from each other slightly more than their own radius. Yet Figs. 3 to 7 have shown that the field of influence of the particles extends well beyond the distance represented by the radius of the particles; thus these effects would tend to be relatively greater in a vulcanizate containing a moderate amount of pigment.



Figure 3

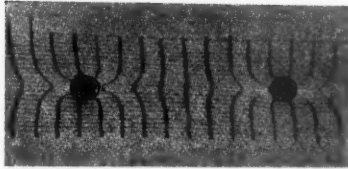


Figure 4

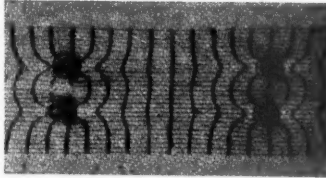


Figure 5

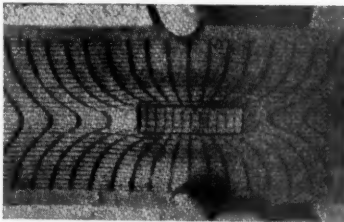


Figure 6

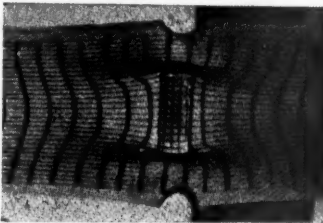


Figure 7

Figures 3 to 7.—Nonuniform Strains Produced by the Insertion of Particles.

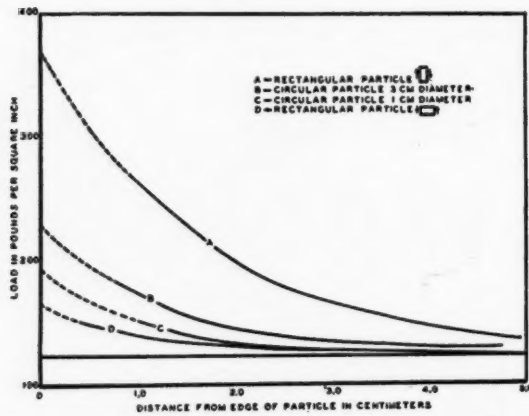


Figure 8—Stress in Pounds per Square Inch vs. Distance from Edge of Particle

From the information accumulated in work with actual pigments in rubber, two general theories have developed. The one, based on abrasion, tearing, and stress-strain studies, assumes that a heterogeneous structure is responsible for reinforcement by increasing stiffness. An attempt to give the mechanism of this action has been made in this paper. The second, based largely on stress-strain measure-

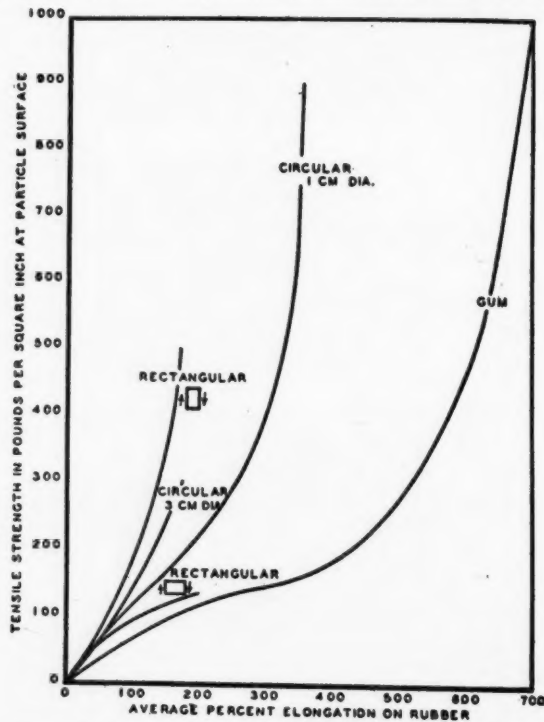


Figure 9—Stress vs. Strain for Various Shapes of Particles

ments and heat of swelling data, explains reinforcement as a surface phenomenon. Among those attacking the problem from the first angle, Haslam⁴ has endeavored to determine which of the various average diameters of a pigment is most significant in determining the physical properties of rubber, and how great an error would

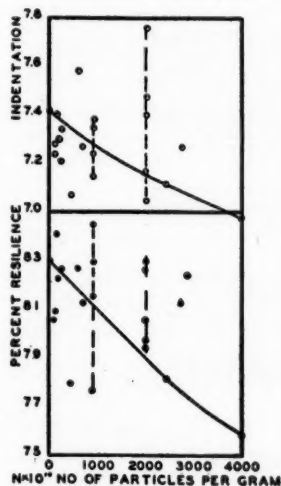


Figure 10—Resilience and Indentation vs. Number of Particles per Gram

result if an average diameter other than the correct one were to be used. Mixtures of four zinc oxide samples of different particle sizes were prepared so that several samples had the same surface area but differed in number of particles per unit weight, while others differed in surface area but had the same number of particles per unit weight. Stress-strain properties, resistance to abrasion, and resistance to tearing were measured. In general, as the specific surface or the number of particles was increased, the reinforcing properties improved, with more effect in the case of specific surface. However, even in the samples in which specific surface was held constant, the physical properties varied somewhat, and these variations were ascribed to variations in uniformity, since they were proportional to the variations between the particle sizes of the component oxides. Table I gives the various diameters, the specific surface, number of particles per gram, and uniformity coefficients of a series of pigments and pigment mixtures prepared according to the method of Haslam, as well as the

equations used in their calculation. A lengthy discussion of these diameters is not justified here, since the subject has been covered by Perrot and Kinney⁵ and by Green.⁶ d_1 is the arithmetic mean diameter, d_3 the diameter, from which specific surface may be calculated, D the diameter, from which the number of

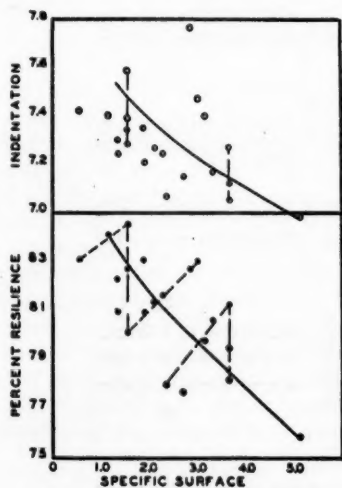


Figure 11—Resilience and Indentation vs. Specific Surface of Particles

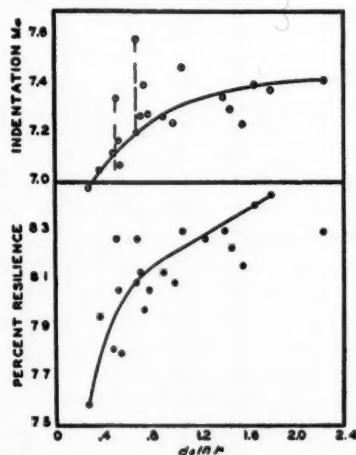


Figure 12—Resilience and Indentation vs. Diameter (d_1) of Particles

TABLE I
VARIOUS DIAMETERS, SPECIFIC SURFACE, NUMBER OF PARTICLES PER GRAM, AND UNIFORMITY COEFFICIENTS OF A SERIES OF PIGMENTS AND
PIGMENT MIXTURES

Equations defining these quantities in terms of the density (ρ), the number of particles of various sizes (n), and the fraction weights of components of mixtures (w).

$$S = \frac{6}{\rho d_s} N = \frac{1}{\rho D_s}, d_1 = \frac{\sum nd}{\sum n}, U d_1 = \frac{\sum d_1 w}{\sum w}, \Delta = \left(\frac{\sum nd^3}{\sum n} \right)^{\frac{1}{3}}, U = \left(\frac{\sum w/d^3}{\sum w/D_s} \right)^{\frac{1}{3}}, d_3 = \frac{\sum nd^3}{\sum nd^2}$$

$$U d_3 = \frac{\sum w}{\sum w/d_s}, D = \left(\frac{\sum nd^3}{\sum n} \right)^{\frac{1}{3}}, UD = \left(\frac{\sum w}{\sum w/D_s} \right)^{\frac{1}{3}}, d_4 = \frac{\sum nd^4}{\sum nd^3}, U d_4 = \frac{\sum d_4 w}{\sum w}$$

Sample	Mixture of	S	$N \times 10^{10}$	d_1	$U d_1$	Δ	U	d_3	$U d_3$	D	UD	d_4	$U d_4$
A	single pigments	5.08	3975	0.132	1.39	0.143	1.55	0.21	1.48	0.165	1.64	0.27	1.25
B		2.36	448	.256	1.16	.314	1.42	.45	1.29	.342	1.38	.53	1.20
C		1.57	107	.44	1.36	.50	1.45	.675	1.4	.55	1.50	.77	1.345
D		.55	4.5	1.28	1.40	1.44	1.53	1.92	1.49	1.59	1.65	2.22	1.385
E	A + B	3.64	2013	.147	1.12	.173	1.21	.298	1.3	.207	1.36	.36	1.54
F	A + C	3.64	2420	.138	1.15	.160	1.27	.293	1.56	.196	1.43	.476	1.31
G	A + D	3.64	2720	.133	1.28	.150	1.43	.293	1.51	.187	1.60	.89	.985
H	A + C	3.30	2014	.140	1.09	.165	1.22	.322	1.35	.207	1.37	.52	1.215
I	A + D	2.84	2013	.133	1.18	.154	1.33	.374	1.32	.207	1.51	1.23	.90
M	B + D	1.57	255	.187	1.01	.226	1.10	.392	1.21	.272	1.23	.50	1.2
N	A + B + D	1.57	606	.162	.87	.208	1.00	.467	1.14	.272	1.14	.67	1.11
L	A + D	1.57	890	.136	.91	.172	1.06	.683	.98	.292	1.23	1.79	.74
J	A + B	2.70	890	.270	1.02	.323	.955	.693	1.35	.292	.93	1.27	1.11
K	A + C	2.27	890	.161	.84	.209	.985	.680	1.08	.309	1.13	1.55	.875

particles per gram may be calculated, Δ is the diameter of the particle of average surface and d_1 the diameter of the particle of average weight. The uniformity coefficients U , were calculated from the following equation given by Green:

$$U = d_1 \left(\sum n/2 \sum n(d_1 - d)^2 \right)^{1/2},$$

in which d_1 is any average diameter, and is introduced to make U independent of magnification and dependent upon the relative values of particle size and the sum of the squares of the "residuals," $n(d_1 - d)^2$. When all the particles are equal in size, U becomes infinite and the average diameters coincide. For mixtures the equation is expressed as a function of the fractional weight (W):

$$\bar{U} = \bar{d} \left(\sum \frac{w}{D^3} / \sum \left\{ \frac{w}{D^3} \left[\frac{d^2}{\bar{U}^2} + 2(\bar{d} - d)^2 \right] \right\} \right)^{1/2}.$$

\bar{d} is used to designate any fixed diameter of the mixture.

An inspection of Table I shows that the d_1 and Δ diameters have little significance in this instance, as for example sample *I*, which is a 50.6:49.4 mixture of sample *A*

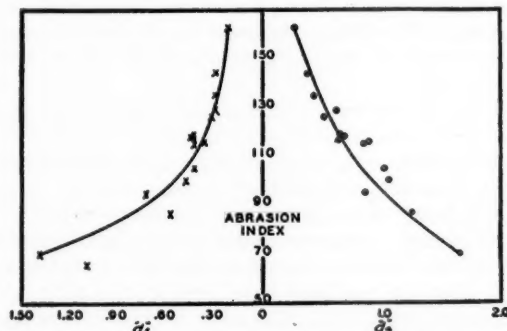


Figure 13—Abrasion Index vs. Diameters d_1 and d_2

($d_1 = .132$; $\Delta = 0.143$) and sample *D* ($d_1 = 1.28$; $\Delta = 1.44$) has a d_1 diameter of 0.133 and a Δ diameter of 0.154. These diameters are actually smaller for sample *I* than for sample *H*, which is a 49.3:50.7 mixture of samples *A* and *C*. The reason is that these diameters are markedly affected by the fine particles and not appreciably by the coarse. Further, the values of the uniformity coefficients of the various mixtures are not in agreement with the uniformity which would be expected from the particle sizes of the components of the mixture. The agreement is satisfactory when the coefficient is calculated on the d_1 diameter, and the next best results are obtained when the d_2 diameter is used, yet even in this case samples $G(A + D)$, and $F(A + C)$ appear more uniform than sample $E(A + B)$.

Lack of space makes it impossible to present all the data obtained on the properties of these pigments in vulcanizates, but Figs. 10, 11, and 12 show some of the results obtained in a rather unusual test, which measures principally the flow properties of the compounds. The formula used was as follows:

Smoked sheet	100
Sulfur	4
Diphenylguanidine	2
Zinc oxide	30 Vol.

These results were obtained with a pendulum which has been described elsewhere⁷ and which measures: (a) resilience, or the percentage of the impact energy returned to the pendulum by the rubber and (b) indentation, the depth of penetration of the hammer-shaped head of the pendulum into the sample. Figures 10, 11, and 12 show the results for resilience and indentation plotted against the number of particles per gram, the specific surface and the d_4 diameter, respectively; the optimum cure for resilience was used in each case.

The agreement between the particle size measurements and the physical properties is obviously better in the last two cases than in the first, and the agreement with the d_4 diameter seems somewhat better than with specific surface. The spread between samples having the same d_4 diameter is as great as between those having the same surface, but in the specific surface curve there are definitely three groups of samples, which if viewed independently would result in the conclusion that resilience and indentation increased with increasing specific surface, a conclusion not warranted in view of the data as a whole.

In Fig. 13, the data given by Haslam, which compares abrasion index with specific surface, have been recalculated to show a comparison of this property with the d_3 and d_4 diameters. The d_4 diameter seems to give a somewhat better agreement with the physical property than does the d_3 diameter or the specific surface calculated from it. For instance, the series of pigments at constant surfaces show a definite trend in size, as indicated by the d_4 diameter, which is in line with the abrasion index.

Perrot and Kinney, in their discussion of the various average diameters, have given a partial explanation of these results. They believe that the d_3 average diameter is the logical one to apply to paint pigments and fillers, since the uniformity of the materials is so high that very little error is introduced. "Consider, however, the pigment 'ranging from ultramicroscopic particles to grains as coarse as sand.' The specific surface of such a pigment would be considerably less than the specific surface indicated by the average diameter, because the relative surfaces of the particles per unit weight of material have been neglected in calculation of this value." It seems very probable that the range of sizes in these synthetic mixtures of pigments involves this error. A number of investigators have endeavored to determine the effect of blending pigments. Dawson⁸ reports that neither combinations of clay and carbon black nor of two zinc oxides follow the mixture law in tensile properties, or hysteresis, either in extension or rebound tests. Lefcaditis and Cotton⁹ found a departure from the mixture law but in the opposite direction, while Beaver and McKay,¹⁰ who also worked with clay and carbon black, obtained values in concordance with the mixture law. If it were possible to measure the proper average diameters of these pigments in the state of dispersion existing in rubber, it might be possible to explain some of these apparent discrepancies.

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- ⁹ Lefcaditis and Cotton, *Trans. Inst. Rubber Ind.*, **8**, 364 (1932).
- ¹⁰ Beaver and McKay, *Ind. Eng. Chem.*, **23**, 294 (1931).

Iron Oxide as a Substance for Increasing the Adhesion of Ebonite to Metal

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Preliminary Communication¹

The literature contains only a few references to the use of iron oxide as a special filler in ebonite mixtures. In discussing the use of ebonite as a dielectric, Khaetzkii,² refers to the German special grade of ebonite, Eisengummi, which gives a very strong adhesion with metal parts, especially iron parts. In contrast to common grades, this ebonite contains iron oxide as a filler. Khaetzkii draws attention also to a modification of "iron rubber," so-called Thermovolt, produced by the Resinotrest.³

Similar brief references to special kinds of ebonite and ebonite cements can be found in the reports of Russian engineers on foreign inspection tours.⁴

In the practice of lining chemical apparatus and rolls, the greatest proportion of defective results is caused by poor adhesion or complete separation of rubber from the metal surface. Therefore greater durability of adhesion of rubber linings, particularly in articles which are subjected to prolonged or even temporary mechanical stresses (rolls, wheels, etc.), is an acute problem in industrial production. Moreover, the nature of the adhesion of materials of such different chemical structure and properties is of considerable theoretical interest.

This preliminary communication is intended to explain the results of an experimental examination of the views on the behavior of iron oxide previously stated.

1. *Method.*—The effect of red iron oxide on the degree of adhesion was studied by laboratory tests of direct rupture by tension (Fig. 1), shear (Fig. 2), and shear plus tension (Fig. 3)⁵ of ebonite cemented to metal with ebonite cement containing different proportions of red iron oxide.

After cleaning and washing the surfaces with benzine, the two iron plates were treated three times with cement and united with calendered ebonite sheet, by the methods shown in Figs. 1, 2, and 3.⁶

The built-up samples were cured in open steam in a digester to the predetermined optimum state of vulcanization.

The mechanical tests were made on a 5-ton Schopper dynamometer equipped with special clamps.

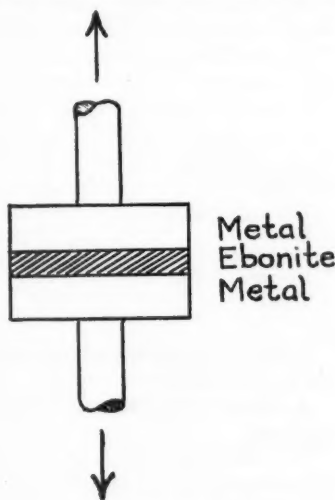


Figure 1

The loads in kilograms per sq. cm. of working metal surface were measured.

2. *Formulas.*—Four cement mixtures were tested: a control *K* and experimental samples *A*, *B*, and *C*, containing 5, 8.2, and 10 per cent of red iron oxide, respectively.



Figure 2

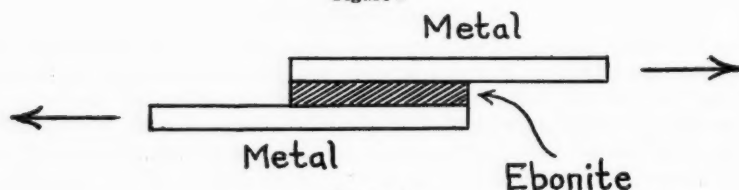


Figure 3

The red iron oxide analyzed as follows: moisture 0.82%, loss after ignition 0.92%, insoluble in hydrochloric acid (1:1) 0.7%, Fe_2O_3 98.1%, SO_3 trace, chlorine trace, reaction of aqueous extract neutral.

RUBBER MIXTURES

Ingredients	Percentages by Weight			
	<i>K</i>	<i>A</i>	<i>B</i>	<i>C</i>
Smoked sheet	41	41	41	41
Sulfur	16	16	16	16
Litharge mixture	2.2	2.2	2.2	2.2
Rosin	0.2	0.2	0.2	0.2
Whiting	40.6	35.6	32.4	30.6
Red iron oxide	...	5	8.2	10.6
Total	100	100	100	100

NOTE: The litharge mixture was composed of: smoked sheet 14, PbO 85, machine oil 1, total 100.

A cement was prepared from each mixture in a laboratory mixer in the usual manner.

For the preparation of the ebonite intermediate layer, two mixtures of the following composition were used:

Materials	Mixture No. 1	Mixture No. 2
Smoked sheet	45-75	19.01
Sulfur	17.35	27.37
Zinc oxide	4	...
Lime	2.28	18.63
Diphenylguanidine	0.54	0.76
Rubrax	1.14	...
Whiting	28.26	...
Pine pitch	0.68	...
Synthetic rubber	...	19.01
Linseed oil	...	2.28
Lamp black	...	1.15
Rags	...	11.79
Total	100	100

The average tests of the adhesive strength of vulcanized ebonite are shown in the following table.

Tests	No. Ebonite	Cement from the Mixture			
Rupture by tension in kg. per sq. cm.	1	46	68	120	114
Shear in kg. per sq. cm.	1	65	85	152	114
	2	80	88	127	119
Shear plus rupture in kg. per sq. cm.	1	61	68	78	74

Conclusions

1. Information from various sources on the increase in adhesive strength between iron surfaces and ebonite brought about by the inclusion of iron oxide in the ebonite was confirmed.

2. In all tests the best results were obtained with ebonite samples No. 1 and No. 2 with addition of 8.2 per cent of red iron oxide (20 per cent based on rubber).

3. Inclusion of 8.2 per cent of red iron oxide in the cement increased the adhesive strength between an iron plate and ebonite 260 per cent measured by the rupture under direct tension as shown in Fig. 1, and 233 per cent measured by the method shown in Fig. 2.

These results were confirmed in factory production. A new formula for ebonite cement containing red iron oxide was developed, which considerably increased the adhesive power.

In conclusion it should be stated that previous to the laboratory experiment, red iron oxide was used for one year in ebonite formulas for magneto parts.

As is well known, most of the parts of a magneto consist of ebonite and cadmium-coated copper armature. However, it has been considered hitherto that red iron oxide acts only as a coloring agent. Red iron oxide is evidently a valuable ingredient for securing strong adhesion between ebonite and metal. Since the Kautchuk factory has adopted the use of red iron oxide in the production of ebonite, the percentage of rejections caused by the separation of armature from ebonite in magnetos had been considerably reduced. This subject requires further experimental confirmation, and the results will be reported in forthcoming publications.

References

¹ For methods of production, application, and properties of red iron oxide, see Chesnokov, *J. Rubber Ind.* (U. S. S. R.), **12**, No. 3, 262 (1935).

² Khaetskii, "Electrical Insulation Materials," **1933**, 284.

³ Though this kind of ebonite is available in the stock of the Krasnui Treugol'nik, the product is in little demand.

⁴ Zmiř, *J. Rubber Ind.* (U. S. S. R.), **11**, No. 2 (1934), and other publications.

⁵ In an ideal case only the cleavage takes place, but, because the dynamometer clamps are in one plane, cleavage plus rupture practically results.

⁶ To avoid rupture of ebonite before the limit of cleaving force becomes effective, the required thickness of the ebonite interlayer was determined by calculation.

Heat Generation and Anisotropy of Rubber Compounds in the Flexometer

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Introduction

In a previous paper¹ a new machine for evaluating the breakdown characteristics of rubber compounds when flexed under compressive loads was described. This machine, which is known as the St. Joe Flexometer, differs from previous flexometers in that the flexing forces can be measured at all times, and the end point is definitely indicated on the machine. With this machine it was shown that when rubber is flexed at a constant horizontal deflection under either constant vertical compression or constant vertical load an increase in flexing force is required to maintain the deflection at a constant value. No attempt was made in the previous paper to explain the phenomenon of the simultaneous occurrence of plastic flow and stiffening of rubber test specimens which was indicated by the data obtained. It was simply pointed out that the data showed good correlation with actual road tests on commercial solid tire and carcass stocks. While a general relationship between heat generation and breakdown time has been indicated^{1,2} a survey of the literature did not disclose any information regarding the phenomena taking place in rubber when flexed under compressive loads. In the present paper a study has been made of the simultaneous occurrence of plastic flow and stiffening action taking place, which has logically led to the investigation of anisotropy.

Description of St. Joe Flexometer

Figure 1 shows a view of the entire machine. Figure 2 is a close-up view of the machine showing the sample under vertical compression and horizontal deflection. Figure 3 is a drawing of the machine, in which the various parts have been labeled.

The test-specimen, which is a cylindrical plug 3.81 cm. in diameter and 3.81 cm. in height, is placed between the two parallel Bakelite face plates and under compression by means of the vertical load weight 6, acting through lever arm 7. The upper face plate is then rotated and the sample, which acts as a coupling, causes the lower plate to rotate. The lower face plate is mounted on the horizontal roller bearing carriage traveling on the track and can be moved off center from the upper plate any given amount by manipulation of handwheel 20. The load required to produce or maintain this horizontal deflection is read on scale 19. The horizontal deflection itself is read on dial 26. By a slight rotation of handwheel 20 the linkage 16 can be lengthened or shortened, thus decreasing or increasing the horizontal load and horizontal deflection on the sample. In this manner it is possible to run tests under constant horizontal deflection (*HD*) or under constant flexing load (*HL*). For a more complete description of the machine the reader is referred to the original article.

Figure 4 shows what happens during a constant horizontal deflection test. The vertical load is maintained constant at 250 kilograms and the horizontal deflection is maintained constant at 0.673 centimeter. The horizontal load, vertical deflec-

tion or compression, and temperature at the center of the test-specimen have been plotted against time. For these and subsequent tests, unless otherwise noted, the following formula was used:

	<i>Parts by Weight</i>
Rubber	100.0
Sulfur	4.0
Di- <i>o</i> -tolylguanidine	1.4
Gas Black	9.0
Zinc Oxide*	150.0

Cure 65 min. at 141.1° C.

* Electrothermic process zinc oxide of medium particle size was used.

Average diameter⁷ by number = 0.26 micron

Specific surface = 1.83 square meters per gram

It will be noted that as the test progresses the vertical compression increases (height of test specimen decreases), which means that the sample is softening and

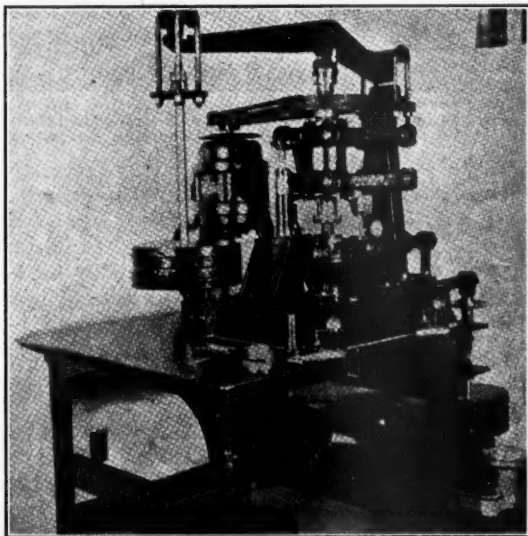


Figure 1—View of the Entire Machine

flattening out. The horizontal load or flexing load, however, increases. This means that as the test progresses the force to produce a given deflection in the horizontal plane increases, indicating a marked stiffening of the rubber. The temperature also increases rapidly during the test, largely from the combined effect of mechanical working and resultant frictional heat, the low heat conductivity and diffusivity of the rubber compound, and in part the Joule effect.

Previous tests¹ carried out under constant vertical compression and constant horizontal deflection conditions show that the increase in horizontal load is not due to a change in the shape of the specimen, but primarily to a structural change or stiffening of the rubber. Evidence of this is presented in Fig. 4A.

Simultaneous Stiffening and Plastic Flow of Rubber

To show how it is possible for rubber to both soften and stiffen in different direc-

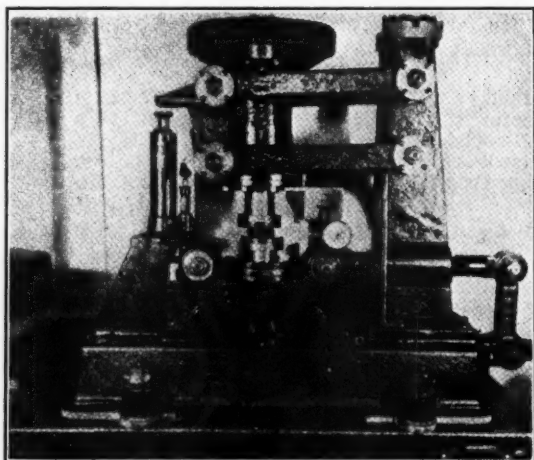


Figure 2—Close-up Showing a Sample Under Vertical Compression and Horizontal Deflection

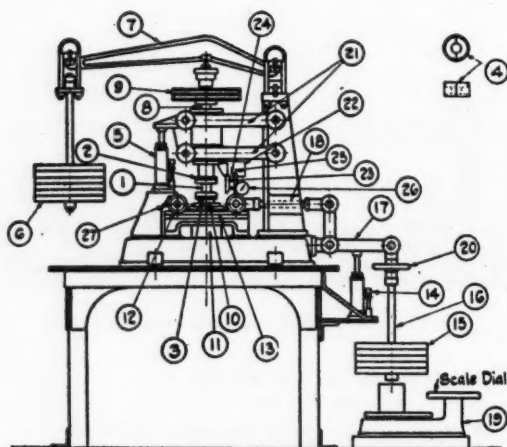


Figure 3—Diagram of Machine

- | | |
|--------------------------|---|
| 1. Rubber test-specimen | 15. Horizontal load weight |
| 2. Upper face plate | 16. Hanger for weights |
| 3. Lower face plate | 17. Bell crank |
| 4. Centering jig | 18. Link |
| 5. Hydraulic jack | 19. Platform scale |
| 6. Vertical load weights | 20. Handwheel for deflection adjustment |
| 7. Lever | 21. Parallel linkage |
| 8. Upper vertical shaft | 22. Double divided scale |
| 9. V-belt pulley | 23. Straight edge for micrometer |
| 10. Lower vertical shaft | 24. Pointer for vertical compression |
| 11. Carriage | 25. Pointer for horizontal deflection |
| 12. Carriage rollers | 26. Dial-type micrometer gauge |
| 13. Track | 27. Carriage stop |
| 14. Hydraulic jack | |

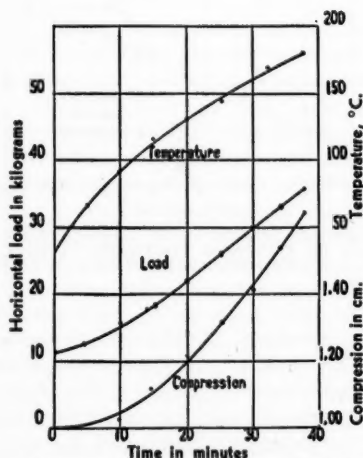


Figure 4—Constant Horizontal Deflection Test. Vertical Load, 250 Kg., Horizontal Deflection, 0.673 Cm.

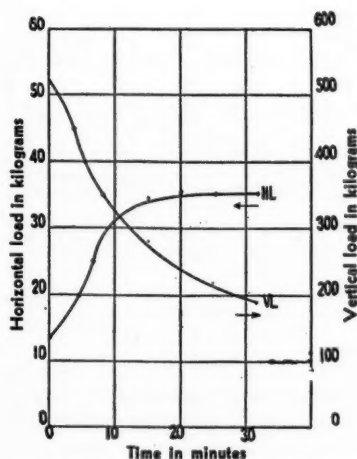


Figure 4A—Constant Vertical Compression Test. Vertical Compression, 1.61 Cm., Horizontal Deflection, 0.714 Cm.

tions at the same time during a flexometer test, it was felt that if stress-strain data could be obtained for various sections of plugs run for different lengths of time in the flexometer, the data would throw some light on what was happening during test. The difficulties encountered in slicing, buffing, and dieing out tensile strips from the regular test-specimens or plugs led to the use of a laminated plug. It was found that a specimen built up of discs (3.81 cm. diameter and 0.19 cm. in thickness) died out from vulcanized sheets would act as a unit in the flexometer, giving results which checked the results obtained by using the regular molded cylindrical plug.

Figures 5, 6, and 7 show tensile strength, 100 per cent modulus (stress at 100 per cent elongation), and elongation at break data for laminated plugs run to 0.1, 0.5, and 0.9 breakdown in the flexometer. The tensile strength before flexing was 185 kg. per sq. cm., modulus at 100 per cent elongation, 46 kg. per sq. cm., and elongation at break, 380 per cent. The results show that during the first part of the test there is a slight increase in tensile strength toward the center of the plug. This is brought about by the cold working at relatively low temperature and is

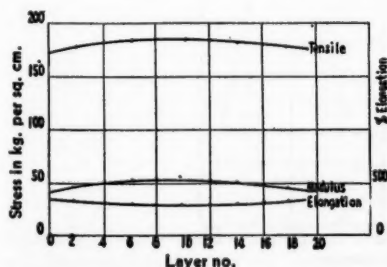


Figure 5—Tensile Strength at 0.1 Breakdown Time

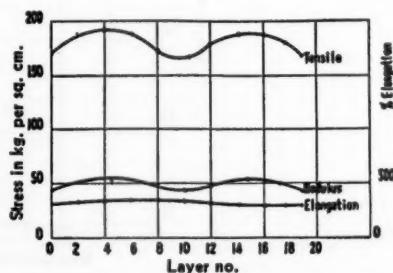


Figure 6—Tensile Strength at 0.5 Breakdown Time

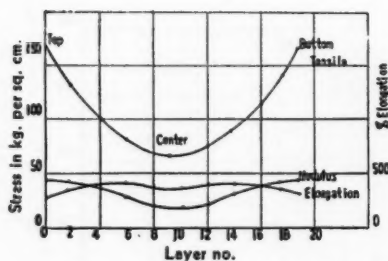


Figure 7—Tensile Strength at 0.9 Breakdown Time

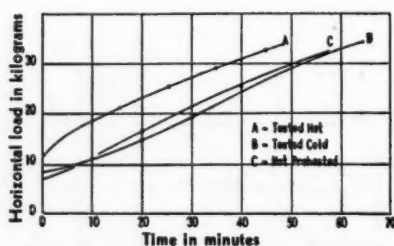


Figure 8—Constant Horizontal Deflection Tests on Preheated Specimens. Vertical Load, 250 Kg., Horizontal Deflection, 0.610 Cm.

probably due to the formation of a new grain structure. As the test progresses, the tensile strength gradually falls off, due to the combined effect of heat, cure, and mechanical working. These effects are greatest toward the center of the plug.

While these data show a slight increase in tensile strength during the first part of the flexometer test, they do not explain the increased stiffening of the specimens as the test progresses. Since the stiffness (as shown by the increase in horizontal load) was measured in the flexometer at high temperature, and the tensile strength was measured at low temperature, it was felt that the increased stiffening might be a heat effect. To confirm this, plugs were heated for 20 minutes and then tested in the flexometer.

In Fig. 8 the horizontal load is plotted against the time for samples preheated

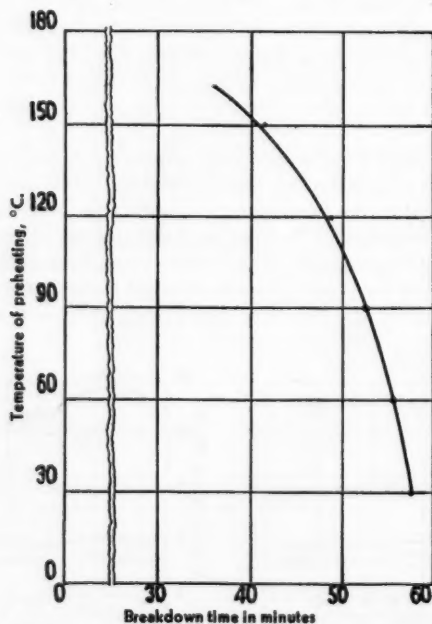


Figure 9—Temperature Preheating vs. Breakdown Time. Vertical Load, 250 Kg., Horizontal Deflection, 0.610 Cm.

at 107° C., and tested while hot and after cooling. The curve for a specimen not preheated is included to show that the additional cure due to preheating causes a lower horizontal load. Similar curves for specimens preheated at other temperatures also indicate that the higher flexing load is a heat effect rather than a cure effect, and is a function of the temperature of preheating. In Fig. 9 the temperature of preheating has been plotted against the time of breakdown only, and it will be noted that as the temperature increases the breakdown time decreases. This relationship holds for tests in which the rate of heat generation is much greater than the rate of heat dissipation, as is usual in the flexometer. In the case of stocks (undercured especially) tested under very low vertical loads and very low horizontal deflections, so that the rate of heat generation approaches that of dissipation, this relationship may not hold true. These results indicate that the

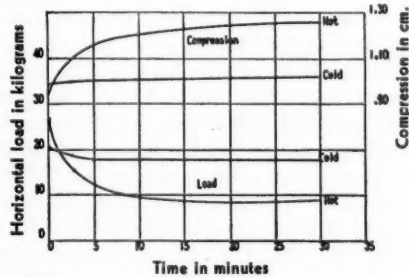


Figure 10—Static Compression Test on Hot and Cold Plugs. Vertical Load, 250 Kg., Horizontal Deflection, 0.714 Cm.

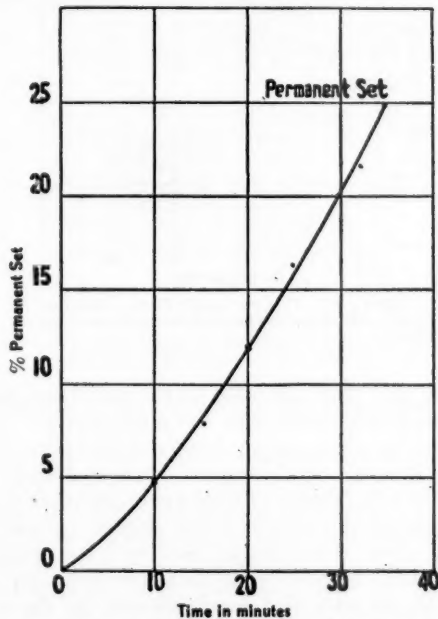


Figure 11—Permanent Set Acquired during Flexometer Test. Vertical Load, 250 Kg., Horizontal Deflection, 0.673 Cm.

stiffening of rubber is mainly a heat effect and that heat has a predominant influence on failure during flexing.

Since the heat generated by mechanical working and possibly the Joule effect has caused stiffening in the horizontal plane, similar stiffening might be expected

in the vertical plane. However, the results of flexometer tests show that during the test the samples actually soften and flatten out, and assume a permanent set. Static compression tests on heated plugs show that for the first ten seconds or so there is a slightly increased stiffness due to heat, but that plastic flow soon sets in and causes the flattening out and resultant permanent set.

Figure 10 shows the data of such a static compression test run on a hot and on a cold plug. The first plug was heated 20 minutes at 157° C., cooled to room temperature, and then tested in the flexometer without rotation under vertical load of 250 kilograms and horizontal deflection of 0.714 centimeter. This plug showed slight evidence of plastic flow, but there was no measurable permanent set at the end of 20 minutes. The other plug was heated 20 minutes and immediately placed in the flexometer under the same static conditions. The curves show that at the beginning of the test of the hot sample there was a stiffening in both the

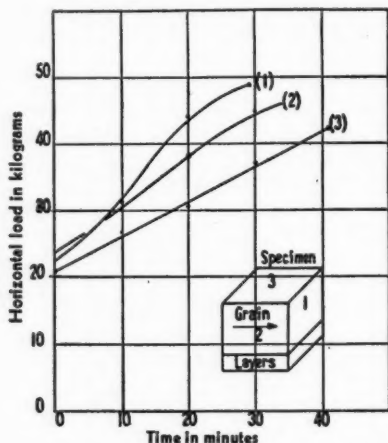


Figure 12—Test on Cubic Plug. Vertical Load, 290 Kg., Horizontal Deflection, 0.760 Cm.

vertical and horizontal planes, as indicated by the initial high horizontal load and low vertical compression compared with the cold sample. After the first few seconds plastic flow set in, as shown by a rapid increase in vertical compression (flattening out of the sample) and decrease in horizontal load. This plastic flow resulted in a permanent set. Figure 11 shows permanent set data plotted against time. These data were obtained by stopping several dynamic tests at different stages of breakdown. Since it was found that the set measured after a 24-hour rest period was very nearly the same as that measured on the hot plugs immediately after the test, only the set after 24 hours is shown. In the dynamic or regular flexometer test the specimen is flexed so rapidly in the horizontal plane (875 r.p.m.) that plastic flow in that plane cannot take place to any substantial degree. In the vertical plane the compressive force acts continuously in the same direction, so that flow does take place. This rapid flexing and reversal of stress in the horizontal plane without flexing in the vertical plane makes it possible for the particular rubber compounds tested to exhibit the simultaneous stiffening and plastic flow.

These data show very definitely that rubber is stiffer at high temperatures than

at low temperatures when plastic flow is substantially eliminated. From thermodynamic considerations also^{3,4} we would expect rubber to be stiffer at increased temperatures. While ordinary stress-strain data⁵ usually show a lower modulus at high temperatures, stress-strain tests made at very high speeds⁶ show a higher modulus for temperatures up to 140° C. Higher modulus could undoubtedly have been obtained on the layers of laminated plugs (Figs. 5, 6, and 7) if the stress-strain tests had been made at a higher speed than is customary with the standard stress-strain machine, and at the temperatures reached in the flexometer test.

Anisotropy

Since rubber compounds when tested in the flexometer exhibit simultaneous plastic flow and stiffening in different directions, it might be expected that pigments having different particle shapes would produce anisotropy of compounds and exert a pronounced effect on heat generation. Since no mention is made in

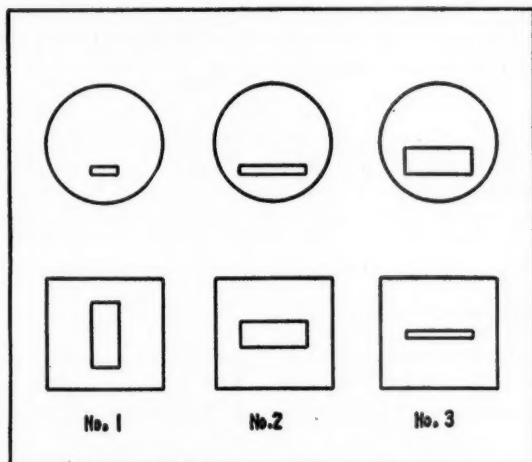


Figure 13—Pictorial Representation of the Orientation of a Rectangular Plate-Shaped Pigment Particle

the literature regarding the effect of anisotropy on heat generation, the following data are presented.

It was first thought that tests could be made on cubes built up from layers each having the grain in one direction. These cubes could then be tested with any one of the three axes in the vertical plane of the machine to show the differences in breakdown characteristics due to "grain" effects and orientation of the pigments.

It might be mentioned here that the resistance to shear of a block of wood along the grain is less than that across the grain, and much less than that perpendicular to the grain. The horizontal load might be considered analogous to the shearing force, and the facing of the test-piece in the flexometer would determine whether shear should occur with, across, or perpendicular to the "grain."

Figure 12 shows results of tests on a 3.81 cm. cube of the same rubber as that used for tests shown in Fig. 4. Numbers at the end of the curves indicate the top face of the specimen during test. Because of unequal stresses in the different directions, considerable vibration was encountered and duplicate results were very hard to obtain. The cubic test specimen was then discarded and the molded

cylindrical specimen was used. To align the pigment particles in different directions, three methods of preparing the samples before vulcanization were used: *Method 1*. The uncured rubber mixture was sheeted out 0.381 centimeter after remilling for two minutes on a laboratory mill (roll temperature 49° C.). After a 2-hour rest period, strips 5.08 centimeters wide, with a length equal to the width

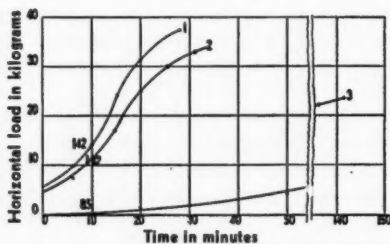


Figure 14—Constant Deflection Tests on Vulcanizate Containing Clay. Vertical Load, 250 Kg., Horizontal Deflection, 0.576 Cm. Curves 1, 2, and 3 Indicate Method of Preparation

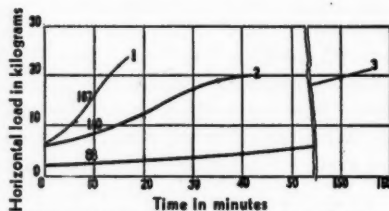


Figure 15—Constant Deflection Tests on Vulcanizate Containing Asbestine. Vertical Load, 250 Kg., Horizontal Deflection, 0.661 Cm. Curves 1, 2, and 3 Indicate Method of Preparation

of the sheet were cut off across the grain and rolled up, making the grain of the rubber parallel to the axis of the cylinder. *Method 2*. In this method strips were cut in the direction of the grain of the sheet and rolled into cylinders. Here the pigment particles were in a spiral perpendicular to the axis of the specimen. *Method 3*. In this method discs died out of the uncured rubber were built into a laminated specimen having the pigment particles in layers perpendicular to the axis.

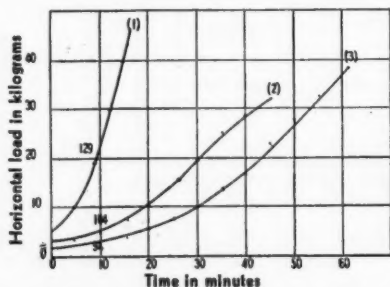


Figure 16—Constant Deflection Tests on Vulcanizate Containing Acicular ZnO. Vertical Load, 250 Kg., Horizontal Deflection, 0.635 Cm. Curves 1, 2, and 3 Indicate Method of Preparation

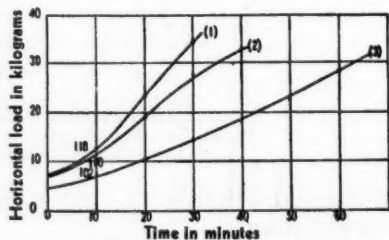


Figure 17—Constant Deflection Tests on Vulcanizate Containing Nonacicular ZnO. Vertical Load, 250 Kg., Horizontal Deflection, 0.661 Cm. Curves 1, 2, and 3 Indicate Method of Preparation

Figure 13 is an exaggerated pictorial representation of the orientation of a rectangular plate-shaped pigment particle subjected to the three methods.

Microscopic examination showed that pigment particles were oriented during milling, with their longest dimension in the direction of milling and their shortest dimension normal to the rolls. Examination showed that this alignment was present after vulcanization. If we consider a pigment having needle- or rod-shaped particles, these particles would be aligned, in method 1, with the long dimension parallel to the axis of the cylinder. In the flexometer the needles would be vertical, and would offer greatest resistance to the horizontal load or flexing

TABLE I. TEST OF VULCANIZATES WITH VARIOUS PIGMENTS

VC = Vertical Compression. HL = Horizontal Load.

Values are given at starting time, at the end of 10 minutes, and at the time of breakdown.

Pigment	Period of Test	Method of Preparation	Time, Min.	VC, Cm.	HL, Kg.	Temp., °C.	Pigment	Period of Test	Method of Preparation	Time, Min.	VC, Cm.	HL, Kg.	Temp., °C.
Clay HD = 0.570 cm.	Start	1	0	1.16	7.0	30	Nonacicular Zinc Oxide HD = 0.661 cm.	Start	1	0	1.16	8.0	30
		2	0	1.14	5.5	30			2	0	1.02	7.5	30
		3	0	1.19	0.0	30			3	0	1.09	5.0	30
	10-min.	1	10.0	1.38	14.8	142		10-min.	1	10.0	1.13	12.7	118
		2	10.0	1.32	11.5	132			2	10.0	1.04	12.2	110
		3	10.0	1.23	1.0	85			3	10.0	1.14	7.8	102
Asbestosine HD = 0.661 cm.	Break	1	27.5	2.14	38.0	216	Magnesium Carbonate HD = 0.508 cm.	Break	1	32.0	1.70	36.0	177
		2	34.5	2.12	35.0	213			2	41.0	1.62	33.0	176
		3	141.0	2.03	23.0	205			3	66.5	1.70	31.5	175
	Start	1	0	1.08	7.0	30		Start	1	0	1.40	9.0	30
		2	0	1.04	6.0	30			2	0	1.35	7.0	30
		3	0	1.08	3.0	30			3	0	1.32	0.0	30
Acicular Zinc Oxide HD = 0.635 cm.	10-min.	1	10.0	1.35	15.0	168	High Gum HD = 1.130 cm.	10-min.	1	10.0	1.94	25.1	174
		2	10.0	1.05	8.0	110			2	10.0	1.86	21.8	168
		3	10.0	1.10	3.0	88			3	10.0	1.52	1.0	121
	Break	1	17.0	1.75	24.0	213		Break	1	16.0	2.24	30.5	208
		2	41.0	1.82	20.0	218			2	16.5	2.21	29.5	207
		3	157.5	1.85	22.0	196			3	40.0	2.20	21.2	192
	Start	1	0	1.14	5.5	30		Start	1	0	1.75	-8.0	30
		2	0	1.04	3.4	30			2	0	1.71	-6.5	30
		3	0	1.12	2.0	30			3	0	1.68	-7.0	30
	10-min.	1	10.0	1.50	21.8	129		10-min.	1	10.0	1.68	-5.7	...
		2	10.0	1.14	5.5	104			2	10.0	1.65	-4.0	...
		3	10.0	1.17	3.4	94			3	10.0	1.63	-4.5	...
	Break	1	16.5	1.93	46.3	200		Break	1	106.5	1.98	26.5	...
		2	45.3	1.90	32.0	198			2	106.5	1.90	23.5	...
		3	61.5	1.98	38.2	182			3	159.0	1.90	23.0	...

force. During the constant horizontal deflection test, we would expect a high horizontal load and a relatively short breakdown time because of rapid heat generation. In methods 2 and 3, the small dimension of the particles would be parallel to the axis of the test-specimen, offering a low resistance to the horizontal load or flexing force, and we would consequently expect lower flexing loads and longer running time in the flexometer test.

If we consider plate-shaped particles with square or round faces, we would expect high flexing loads with short breakdown times in methods 1 and 2, where the larger dimension of the particle is parallel to the vertical axis, offering greater resistance to the flexing load. In method 3, the plates would form a laminated structure, in which the thickness of the particle would be parallel to the vertical axis, and we would expect a much lower horizontal load and much longer breakdown time.

If the pigment particles are rectangular plates, we would expect method 2 to give a lower flexing load and longer breakdown time than method 1. Method 3

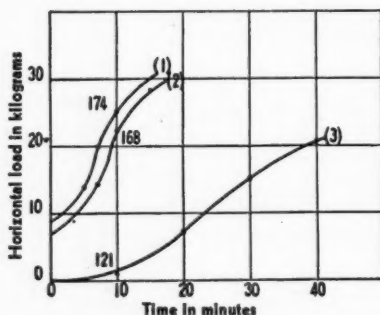


Figure 18—Constant Deflection Tests on Vulcanizate Containing Magnesium Carbonate. Vertical Load, 250 Kg., Horizontal Deflection, 0.508 Cm. Curves 1, 2, and 3 Indicate Method of Preparation

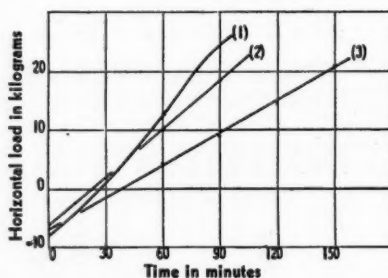


Figure 19—Constant Deflection Tests on "Pure Gum" Vulcanizate. Vertical Load, 215 Kg., Horizontal Deflection, 1.130 Cm. Curves 1, 2, and 3 Indicate Method of Preparation

would give much lower flexing load and considerably longer running time than method 2.

In order to check this theory, the formula referred to above with all but one volume of zinc oxide replaced by equivalent volume loadings of magnesium carbonate, clay, Asbestine, acicular zinc oxide and nonacicular zinc oxide was used. These vulcanizates were tested in the flexometer with a constant vertical load of 250 kilograms and constant horizontal deflections indicated on the graphs.

Figures 14, 15, 16, 17, and 18 show the horizontal load-time curves obtained in the tests. The temperatures at the center of the test-specimens after 10 minutes of flexing are indicated along the curves. The method of preparation of the plug, which indicates the grain direction, is given by the number at the end of each curve. A vulcanizate without pigment is shown in Fig. 19 for comparison. In this case temperature measurements were not made, to eliminate any possible tendency of the hypodermic-needle thermocouple to cause premature failure. Vulcanizates containing no filler or pigment generally have a tendency toward mechanical failure. Table I includes time, vertical compression, horizontal load, and temperature data for each test at the start, after 10 minutes, and at the breakdown point.

Flexometer tests on vulcanizates containing clay (Fig. 14) show that the break-down characteristics of specimens prepared by methods 1 and 2 are very similar, while in those prepared by method 3 the horizontal load is lower and the running time considerably longer, with slow heat generation. These data indicate that the particles are thin plates.

In the case of vulcanizates containing Asbestine (Fig. 15), differences in break-down characteristics between specimens prepared by methods 1 and 2 are very pronounced. This indicates that the length of the particle is considerably greater than the width. The very low flexing load, long time, and slow heat generation of specimens made by method 3 indicate that the thickness of the particle is considerably less than either the length or width. In effect, the particles of Asbestine act as if they were long thin needle-like crystals or ribbons.

The curves for vulcanizates containing acicular zinc oxide (Fig. 16; the oxide used being an American process product having an average diameter⁷ of 0.36 micron and a specific surface of 1.54 sq. m. per g.) show that specimens made by method 2 run for a much longer time under a lower flexing load than specimens made by method 1. These data indicate that the length of the particle is much greater than the width, and the similarity of the curves for specimens made by methods 2 and 3 show that the thickness is about the same as the width, indicating a close approach to the true needle shape.

For nonacicular zinc oxide (Fig. 17) the data indicate a more nearly isotropic shape.

The results of these tests enable the prediction of particle shapes which agree fairly closely with those shown by microscopic examinations of the pigments used. However, breakdown characteristics of plugs made by method 3 show greater differences from characteristics of methods 1 and 2 than would be predicted by the theory and microscopic studies. These differences would indicate anisotropy of the rubber hydrocarbon itself, and the curves for the vulcanizate without filler (Fig. 19) show evidence of such anisotropy, which may possibly vary in its effect with different pigments in compounded mixtures. This long running time of specimens prepared by method 3 is due in part also to the fact that the vulcanizate is approaching the point at which heat dissipation is as rapid as heat generation.

As a further confirmation of the theory, flexometer tests were run on a vulcanizate containing magnesium carbonate. From the curves of Fig. 18, a thin plate-shaped particle was predicted. This shape differs from the usual one which is needle-like, but a microscopic examination revealed that the plate type of particle was actually predominant.

While the data in general substantiate the theory, which is based on particle shape, there is evidence of other factors which enter into the picture, so that quantitative predictions cannot be made. Several of these factors are "skin" effect in the laminated plugs, possible lack of complete alignment of particles during milling, and variable anisotropy of the rubber itself in different compounds. There is also microscopic evidence of a breaking up of some of the pigment particles during test.

Conclusions

Data have been presented to show that it is possible for rubber compounds when tested in the flexometer to exhibit simultaneously a plastic flow in one direction, and a marked stiffening in another direction, resulting from the elimination of plastic flow by rapid flexing. Both effects are shown to be due mainly to heat generation or temperature effects. The rate of heat generation depends in part on the anisotropy of the rubber, which is much greater than is indicated by some

of the ordinary physical tests such as tensile strength, resistance to tearing and to abrasion. The theory that the degree of anisotropy is influenced by the shape and orientation of the pigment particles and of the anisotropy of the rubber itself has been in a measure experimentally verified.

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The Use of Factice in Rubber Manufacture

E. H. Hurlston

The two main classes of vulcanized oil substitute or factice are heat-cured brown factice and cold-cured white factice. They were both introduced into the rubber industry at about the same time (1846-1847), the former variety by Anderson and the latter by Parkes. It has been stated (Twiss, *Trans. Inst. Rubber Ind.*, 7, 234 (1931)) that Parkes first opened a proofing factory at Birmingham but that the business was shortly afterwards absorbed by Chas. Macintosh & Co. and transferred to Manchester. This probably dates the commencement of the use of white factice in proofings. The early history of the development of the use of brown factice on a works scale is more obscure.

As the name implies, these vulcanized oils were used in the first place as ingredients which could economically substitute part of the crude rubber content of mixings, but as time went on it became apparent to compounders that these materials possessed intrinsic properties which made them almost indispensable in certain mixings, both for ease of manufacture and for high quality of the resultant article. The utility of factices in the general rubber trade is therefore in many respects analogous to that of reclaimed rubbers.

Although these oil factices still fall into the two main classifications of heat-cured and cold-cured, many varieties now appear on the market, each characterized by special properties which make it suitable for certain purposes.

Cold-cured factices, known also as white substitutes, are used for the most part in mixings which are themselves vulcanized by means of sulfur chloride, examples being single texture proofings and thin calendered sheet articles, but there are also applications in some heat (sulfur) cured goods such as erasers, bed sheets, and certain moldings. White factice should be of a good color and it should also have a sweet odor, fine particle size, and good springy texture. The last-named property is rather difficult to express, but it can easily be tested by placing samples from different makers side by side on a piece of paper and comparing the texture with the fingers. It is also important that the material should not deteriorate when kept for a period in a stoppered bottle (*India Rubber World*, 4, 305 (1891)). These properties will depend to some extent on the degree of vulcanization of the oil which is estimated by means of extraction with a solvent such as acetone. The acetone extract (cold) varies between 2 per cent and 10 per cent and is rather higher in the case of eraser factice. The mineral matter of white factice as estimated by the ash content is generally about 1 per cent and consists for the most part of the residue from alkaline metallic salts such as magnesium oxide, magnesium carbonate, or sodium carbonate, which are added during manufacture to neutralize any development of acidity.

As mentioned previously, the chief use of white factice is as a major ingredient in cold-cured, single texture proofings. The amount varies according to the class of proofing, amount of mineral loading, and the effect which is desired, but in general it may be said to lie between one-half to the full proportion of crude rubber used. The presence of the factice improves the finished material in many ways. It confers flexibility, silky finish, and good aging properties (Lloyd, *Trans. Inst.*

Rubber Ind., 3, 52 (1927)). These effects may be closely related, as it is thought by many that the use of factice improves the penetration of the cold-cure vapor or fluids into the rubber compound, thus giving a more even cure throughout.

The article which probably contains the highest proportion of factice to rubber is the eraser. It is not uncommon for a pencil eraser to contain as much as two

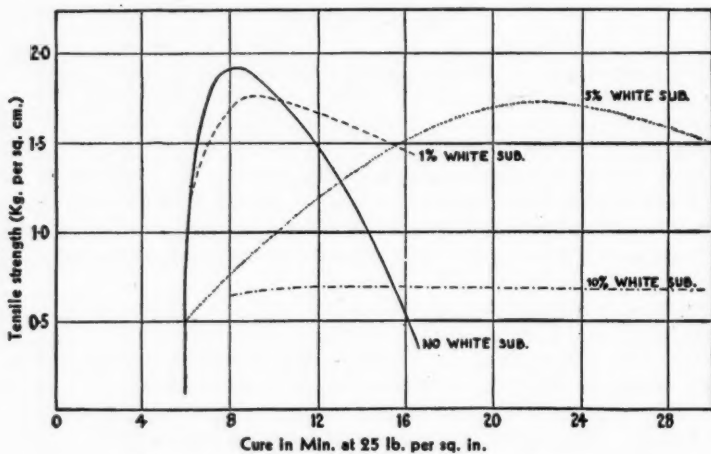


Figure 1—Effect of White Factice on Rate of Cure

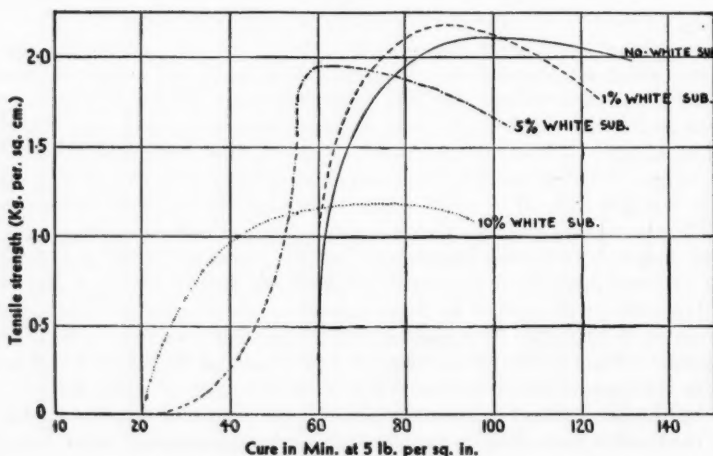


Figure 2—Effect of White Factice on Rate of Cure

to three times as much white factice as crude rubber. In these proportions the desirable crumbly nature is induced in the material. For soft erasers a proportion of a special sticky white factice is frequently employed.

In heat-cured articles the use of white factice is much restricted by the retarding effect which it exerts on vulcanization. This is generally considered to be due to

acidity developed during cure, and to offset this, alkaline materials, such as lime and magnesium oxide, are commonly added to the mixings.

The retarding effect on the curing properties of rubber has been made of use in reducing the tendency to scorch of mixings containing ultra-accelerators. One or two per cent on the rubber is sufficient to make a definite difference in this direction. The effect is not, however, universally applicable, as the experimental results of tests with the following more common fast accelerators will show.

BASE: PALE CREPE, 100; SULFUR, 3; ZINC OXIDE, 3; STEARIC ACID, 1; ACCELERATOR, 1

Accelerator	P. P. D.	Z. I. X.	Z. D. C.	M. B. T.	T. M. T.	T. E. T.	$\frac{1}{2}$ M. B. T. + $\frac{1}{2}$ D. P. G.
			Scorch at 220° F. (min.)				
Base	5	3	9	33	40	70	10
Base + 2%	5	18	37	70	40	70	14
White Factice							

It will be seen that the retarding or anti-scorching effect is most marked with the use of mercaptobenzothiazole (M. B. T.), zinc diethyldithiocarbonate (Z. D. C.) and zinc isopropylxanthate (Z. I. X.). The mixture of equal parts of mercaptobenzothiazole and diphenylguanidine ($\frac{1}{2}$ M. B. T. + $\frac{1}{2}$ D. P. G.) is affected to a less extent, whereas piperidine piperidylthiocarbonate (P. P. D.), tetramethylthiuram disulfide (T. M. T.) and tetraethylthiuram disulfide (T. E. T.) are not affected at all, indeed other tests have shown a slightly greater tendency to scorch when white factice is added.

This effect of increased scorchiness after addition of white factice is at variance with the generally accepted view that white factice retards vulcanization. The explanation appears to lie to a great extent in the temperatures employed for vulcanization.

The physical test data given in Figs. 1 and 2 were obtained on a series of mixings, containing rubber, 100; sulfur, 3; zinc oxide, 3; stearic acid, 1; tetramethylthiuram disulfide, 1; and increasing amounts of white factice, which were vulcanized at two different temperatures corresponding to 5 lbs. and 25 lbs. per sq. in. steam pressure.

It will be seen that at the lower temperature (Fig. 2) there is an acceleration of the cure by addition of white factice, whereas at the higher temperature (Fig. 1) a retardation of cure, associated with lower tensile properties is apparent. The retarding effect is probably due to a breakdown of the white factice at higher temperatures, as suggested by previous writers (Baker, Bodger, and Cotton, *Trans. Inst. Rubber Ind.*, 7, 144 (1931)); the acceleration at low temperatures may be due to the free alkali, or to sulfur compounds present in the factice.

Most factices have an accelerating action on a mixture vulcanized wholly with tetramethylthiuram disulfide, or at any rate increase its tendency to scorch at high milling temperatures. The following figures illustrate the effect obtained by adding the factices specified to a base mixture containing pale crepe rubber, 100; tetramethylthiuram disulfide, 3; zinc oxide, 3.

Type of Factice	Time to Set Up at 220° F. (Min.)
	Factice
Base	130
2 per cent White	125
2 per cent Light brown	120
2 per cent Dark	98
2 per cent Vulcatac	87
10 per cent White	70
10 per cent Light brown	50
10 per cent Dark brown	45
10 per cent Vulcatac	60

Other heat-cured articles, in which white factice is used, are wrapped bed sheetings, wringer rollers, and some steam-cured extruded moldings, though in all these goods the material is rapidly losing ground in favor of the lighter colored varieties of brown factice. Undesirable effects produced by white factice which militate against its use in most heat-cured goods are deadness of the mix, poor abrasion resistance, and increased water absorption.

Brown factice is not so detrimental in this respect. Heat-vulcanized oil comes on to the market in several distinct varieties. There is dark brown factice with a combined sulfur content of 15 to 25 per cent and acetone extract (cold) of 15 to 20 per cent; a paler colored variety of light brown factice represented by such brands as "Whitbro" and "Gloria," with total sulfur of 20 to 25 per cent and acetone extract varying from 10 to 25 per cent; and the special varieties described by Auer (*Trans. Inst. Rubber Ind.*, 4, 499 (1928)), represented by the Vulcatac range which have an acetone extract of about 30 per cent and total sulfur of 10

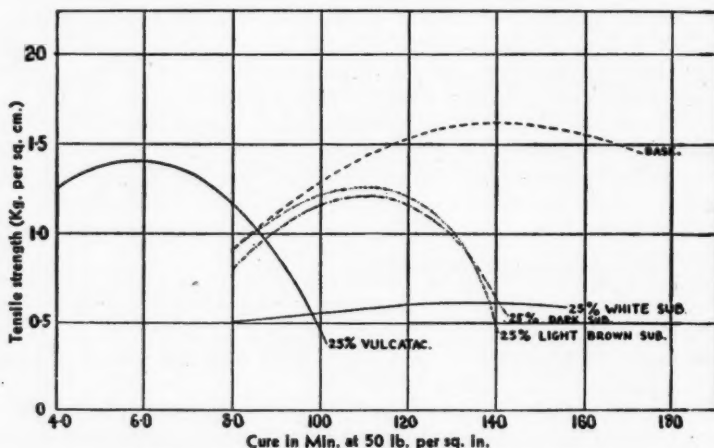


Figure 3—Effect of Factice on Tensile Properties

per cent. These are characterized by powerful softening effects on the mixture, with good tensile strength and resiliency in the vulcanized product. A still further development is a water dispersed factice, specially prepared for use with latex.

Brown factices are employed almost exclusively in heat-cured goods, the principal applications being open-cured tubing and packing strips, soft hose linings, double texture proofings, soft rollers, sponges, and wrapped steam-cured sheetings. For such goods as are formed on the tubing machine or extruder the inclusion of brown factice in the mixing has been found to give a smooth surface, to reduce swell from the die and hence to give an even gage, and also to assist in holding up the material in the uncured state. These effects can of course be achieved by the use of a reinforcing filler such as magnesium carbonate or china clay, but at the expense of hardening the finished vulcanized article.

To illustrate the effects of various factices on the plasticity of mixings, the following comparative test results were made with mixtures of varying amounts of the materials with pale crepe rubber.

The tests were made on the extrusion type of plastometer (Griffiths, *Trans. Inst. Rubber Ind.*, 1, 308 (1926)), load 500 lbs., die $\frac{9}{16}$ th in., die angle 50° , temp.

85° C., the times of mixing, roll temperatures, etc., being maintained as constant as possible. The plasticities were as follows:

Per Cent Factice	White Factice	Dark Factice	Light Brown Factice	Vulcatac
0	2.6
1	2.4	1.7	2.2	1.3
5	2.3	1.4	2.0	1.1
10	2.3	1.0	1.4	0.8

It will be observed that white factice has very little effect on plasticity, measured in this manner, whereas the effect of Vulcatac is most marked.

In a mix containing rubber, 100; and sulfur, 10; the Vulcatac type shows a marked acceleration, the other brown varieties show the effect to a less extent, whereas the white factices show retardation. These results are shown in Fig. 3.

Tests have indicated that brown factices can be used in a gas black mix such as used for belt and hose covers in amounts up to 5 per cent on the rubber content without adversely affecting tensile strength, stretch and tear-resistance properties. However, abrasion tests revealed a gradual falling away of wear-resisting properties with increasing proportions of factice. This result was not unexpected, but was of interest in showing that tensile strength and stretch tests, taken alone, do not give a true indication of the wear-resisting properties of the mixings.

In conclusion, the author wishes to express his thanks to colleagues for help given in preparation of this paper, and to the Dunlop Rubber Company, Ltd., for permission to publish the results of tests.

The Pendulum as a Source of Energy for Plasticity Measurements

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ADVANCEMENT in methods for studying the consistency of rubber during the last 10 years has been confined largely to various modifications of previous tests and to better interpretation of the data obtained.

The extrusion plastometer introduced by Marzetti (11) has been modified by Behre (1) to provide a battery of instruments, by Dillon and Johnston (5) to provide more simple apparatus capable of operating at increased rates of shear, and by Dillon (4) to provide an instrument for rapid control work. The parallel-plate plastometer (16) has received numerous modifications of form. DeVries (2) modified the plates to provide a constant area of contact with the rubber. This modification was used by van Rossem and van der Meyden (14) who stressed the necessity of following the elastic recovery as well as the rate of compression. Karrer (8) pointed out the need for controlling the time factor during compression and recovery and has described an instrument (9) with which each measurement requires about 30 seconds. The balance plastometer, which employs parallel plates, was described by Hoekstra (7) and is well adapted to following the elastic recovery after the rubber has been compressed under any conditions of thickness and time. A parallel-plate instrument with interchangeable parts to provide various methods of applying pressure and following recovery was described by Lefeaditis (10). The relation between compression and the extent of recovery has been considered by Dillon (3), who concluded that the measurement of either the compression or the elastic recovery as obtained with the usual parallel-plate plastometer was sufficient if the comparison was confined to a number of batches of a given stock or type of rubber. He also pointed out that elastic recovery depends on the speed of the previous deformation. Hoekstra (6), after considering some of the factors involved in plastic flow, concluded that elastic recovery should be measured only after compression of a rubber to the fixed thickness. The general usefulness of the parallel-plate plastometer has been greatly increased by the mathematical treatment of Peek (13) and Scott (15).

A third type of plastometer, consisting of a disk which rotates in compressed rubber while the resistance to shear is measured, has been described by Mooney (12).

General Considerations

Manufacturing difficulties are more often due to the elasticity of rubber than to its resistance to flow. Materials such as lead are easily extruded or rolled into a form which is retained. On the other hand, rubber, after being deformed, never retains its shape perfectly and careful control

is required to prevent excessive and sometimes irregular deformation.

The volume flow per unit volume of a material is unlimited. If the flow takes place in an orderly manner, such as that resulting from compression between parallel plates, the total displacement and shear can be determined. If the flow takes the form of internal rearrangement without change of external shape, the shear and displacement usually cannot be determined. An example of the latter type of flow is the mixing

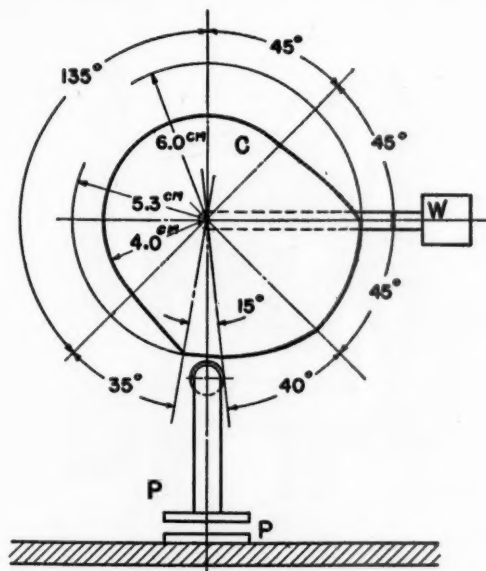


FIGURE 1. DIAGRAM OF APPARATUS

of a rubber cement by a paddle immersed in the cement. Both types of flow are unlimited in extent and produce either thorough mixing or very great changes in shape.

On the other hand, the amount of elastic strain in rubber is definitely limited and is a direct result of shearing resistance. The frictional resistance between either elastic particles or plastic and elastic particles in relative motion causes the elastic particles to be strained. The strain increases for any rate of shear until the resulting stress is equal to the frictional resistance, after which no further strain can be produced. The elastic strain will then reach a maximum after sufficient shear has taken place, the exact amount being a function of the elastic properties and resistance to flow of the rubber.

Since recovery depends on the residual elastic strain at the time flow ceases, it follows that elastic recovery will also be some function of the resistance to flow of the rubber. The

consistency of rubber would then seem to be determined equally well by measuring either the resistance to flow or the recovery. This may be approximately true if only one grade of rubber is considered. When different types of compounded or uncompounded rubber or other types of material are considered, the relationship between resistance to flow and elastic strain does not remain constant. For this reason, it is neces-

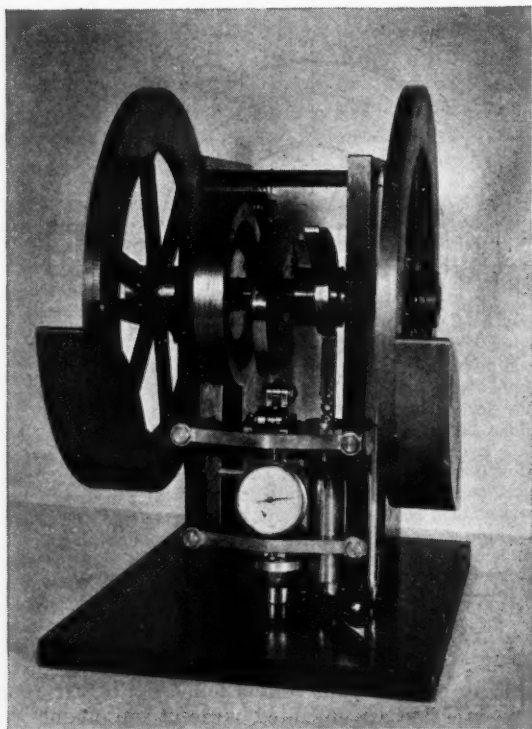


FIGURE 2. PHOTOGRAPH OF INSTRUMENT

sary to determine both resistance to flow and elastic recovery in each case. The measurement of elastic recovery should be made only after shear sufficient to produce an equilibrium stress. In order to produce a reliable index to the working quality of the material, the deformation should produce a rate of shear comparable to that existing in service.

Description of Apparatus

The energy required to produce a definite deformation can be supplied by a pendulum which will also control the time within limits. The quantity of energy required can then be

determined from the damping effect produced on the pendulum. The general form of such an instrument is shown in Figure 1. A pendulum, *W*, of known potential energy is brought to rest in a horizontal position. When released, it actuates a cam, *C*, which serves to compress the rubber between parallel plates, *P*. After the pendulum reaches the lowest point the cam rapidly releases the upper plate in order that the elastic recovery may be followed. The pendulum continues its swing and is maintained in position at its maximum height. The amount of energy consumed in the cycle is proportional to the cosine of the angle which the pendulum described in its upward swing.

The instrument which has been designed is shown in Figure 2. The pendulum consists of two weights of 2630 grams each, the center of gravity being on a radius of 7.3 cm. Each weight is attached to a balance wheel of 3710 grams, the combined moment of inertia of which gives the system a period of 0.6 second for a complete vibration. The shaft connecting the two balance wheels carries the cam which actuates the upper plate, a ratchet for maintaining the position at any point on the upswing, and a cam which works against a dash-pot and lowers the system to the correct starting position. The driving cam can be replaced by others of different shape for special work. The weight of the upper plate assembly, under which the recovery must take place, is 300 grams. To compensate for the mechanical inefficiency of the system, the pendulum is dropped from 2° above the horizontal position and a complete cosine scale is inscribed on the face of one balance wheel to cover the upswing from the low point to 2° below the horizontal. The wheels rotate with the top moving toward the rear.

Operation is as follows: The instrument is enclosed in an oven which maintains the desired temperature. A forward position of the weights permits the upper plate to be raised sufficiently for inserting the test sample, which is 1 cc. in volume, approximately 10 mm. long, and should be approximately cylindrical. The sample should be preheated for at least 10 minutes before being tested. The weights are then raised to the highest position from which they lower slowly under control of a cam and dash-pot to the starting position. During the descent of the weights to the horizontal, the sample is compressed to a thickness of 7 mm. The weights are then released. During the next 45° rotation the sample is compressed to a thickness of 1.25 mm., at which thickness it is held for an additional 45° before being released. The cosine of the angle of upswing is read and the recovered thickness is recorded after equilibrium is reached, which often requires less than 15 seconds. Highly elastic materials show a slow elastic creep toward the end of their recovery which amounts to a few per cent of the total. In this case the recovery is usually read after an arbitrary time.

The energy consumed should vary with duplicate samples by not more than ± 1 per cent and the recovery should fall within ± 5 per cent of the actual recovered height.

The enclosure of the test sample between sheets of paper can be the cause of nonuniform results. The sample after compression adheres tightly to the paper and must deform the paper in order to recover any portion of its former shape. Heavy paper requires a large amount of energy for the de-

formation and produces irregularly projecting wrinkles. Thin, porous paper stretches and slips against the plates during compression by an amount which varies with the resistance of the rubber and disturbs the type of flow produced. If paper is used, the type must be standardized, and unmarked cigaret paper should probably be preferred. Clean test pieces, without paper, talc, or other lubricant, unless excessively tacky, cause no difficulty. Materials such as asphalt and wax which adhere to metal should be run against removable thin metal plates, since the resistance to flow of these materials at high rates of shear is sufficient to tear paper.

The amount of compression adopted was shown by experiment to produce sufficient flow to provide a maximum elastic recovery for most samples of rubber. Very soft rubber tested at 70° C. gave a maximum recovery if compressed from any thickness greater than 2.5 mm., while tough rubber required compression from a height of at least 6 mm. down to the final thickness of 1.25 mm.

TABLE I. CHANGE IN CONSISTENCY OF RUBBER WITH MILLING

Min- utes Milled	Pendulum Plastometer, 70° C.			Parallel-Plate Plastometer, 70° C.		
	Available energy con- sumed %	Thickness re- cov- ered ^a Mm.	Re- covery %	Thickness after 5 minutes Mm.	Recovered thickness ^a after 1 minute Mm.	Re- covery %
5	55.6	6.85	548	5.35	7.12	33.1
	53.8	6.40	512			
	54.5	6.82	546			
10	51.0	5.15	410	4.27	5.47	28.2
	50.2	4.95	396			
	52.0	4.98	399			
15	48.6	4.57	366	3.95	4.96	25.6
	50.0	4.34	347			
	49.0	4.65	372			
20	49.0	4.52	361	3.71	4.50	21.3
	46.7	2.73	218			
	46.8	3.10	248			
30	48.0	2.96	237	3.30	3.81	15.5
	46.7	1.55	124			
	45.8	1.64	131			
45	45.7	1.55	124	2.82	3.26	17.0
	46.7	1.49	119			
	44.8	0.92	73			
	44.8	0.96	77			

^a Thickness recovered is the increase in thickness from the thickness of greatest compression. Recovered thickness is the total thickness of the sample.

The amount of energy available for compressing the rubber depends on the shape of the cam. The cam described compresses the rubber during only the first 45° rotation of the pendulum, which limits the amount of energy available to the cosine of 45° times the potential energy of the pendulum at the starting position or to a reading of 70.7 on the instrument scale. The substitution of a cam which compresses the rubber through an angle of 90° would make available the total potential energy of the system.

Experimental Part

The type of results obtained with the pendulum plastometer is illustrated by the following experiment. Two thousand grams of pale crepe rubber were milled on a 45×20 cm. mill, through which water at 50°C. was circulated. The temperature of the rubber was approximately 70°C. during the milling. Samples were removed at intervals for test. The consistency of the rubber was followed by means of both the pendulum plastometer and the parallel-plate plastometer (16). The results are shown in Table I. Several sets of data are shown with the pendulum instrument, in order to illustrate the degree of duplication. The samples run in the pendulum plastometer were in direct contact with the metal plates.

TABLE II. ENERGY CONSUMPTION AND ELASTIC RECOVERY

Material	Available Energy Consumed	Thickness Re- covered	Recovery
	%	Mm.	%
Rubber 100, mineral oil 30	24.8	0.53	41.4
Rubber 100, mineral rubber 50	37.5	0.41	32.8
Mineral rubber (0.5-cc. sample)	68.0	0.07	5.6
Tire tread stock	67.0	4.03	322.0
Balata	57.3	0.54	42.1

The data obtained with the two instruments are directly comparable only in regard to the elastic recovery. The pendulum instrument shows not only a much higher recovery, but a much greater difference between the extremes. The thickness index of the parallel-plate plastometer, while not indicating a quantitative energy relationship, has a greater percentage spread than the energy consumed by the pendulum instrument. The thickness index is probably satisfactory for following the uniformity of a given material. The energy consumed should, however, be a more reliable index for a comparison of various rubber compounds or other materials.

While a more or less definite dependency exists between the elastic recovery and energy consumed by different samples of the same rubber, this relationship varies considerably when different rubber compounds or other substances are considered. This is illustrated by the data in Table II, which shows the results of tests on various compounds and substances.

The early stages of vulcanization are detected with the pendulum plastometer by the rapid change in the elastic recovery. In many cases the elastic recovery will double before a noticeable difference is found in the energy consumed.

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Bacterial Decomposition of the Rubber in Hevea Latex

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A RECENT communication (6) has shown by several different means that rubber present in the living plant actually disappears under seasonal and other conditions in the life of the plant, and that it can, therefore, no longer be regarded as an excretory product of metabolism of no physiological value to the plant. The results recorded were obtained in a study of the rubber content of *Parthenium argentatum*, but they will undoubtedly be found to hold for *Hevea brasiliensis* when suitable methods of investigation are developed for the latter.

The importance of these findings in relation to the economic development of rubber is obvious and far-reaching. They have already been applied in the cultural development and exploitation of *Parthenium argentatum*.

On the scientific side they suggest a more intimate study of the behavior of the rubber hydrocarbon towards oxidation-reduction processes occurring within the living plant and to the effect of such agencies on the rubber itself *in vitro*. That rubber is readily attacked by oxidizing agents in general is now well known. But even the classical researches of Harries on the products of decomposition of the rubber hydrocarbon by means of ozone (1) have thrown little light on the ways and means by which the rubber in the plant is first produced and thereafter broken down and utilized in its cycle of yearly development. This is not surprising when we consider the reagents heretofore employed and the drastic character of the decompositions effected by them.

The solution to this question will probably be found in microbiological methods. Therefore, this investigation had as its object, first to determine the extent to which the rubber hydrocarbon is affected, directly or indirectly, by the action of bacteria, and subsequently to study the nature of the changes brought about by these means and by the extracellular enzymes developed therefrom. The present paper will give the first account of some striking results obtained on the decomposition of the rubber hydrocarbon of Hevea latex by means of bacteria under aerobic conditions; a subsequent paper will show how the physical character and quality of the rubber from *Parthenium argentatum* is profoundly

changed, for better or for worse, by decomposition of the cortical tissue by means of pure cultures of certain organisms under anaërobic conditions.

We would hardly expect that a solid, compact mass of rubber in its coagulated state would be subject to bacterial action to the same extent as the same material in the finely dispersed condition in which it exists as latex in the plant. This probably accounts for the fact that little progress has been made since the original work of Söhngen and Fol (2) who showed that species of *Actinomyces* developed on thin films of rubber on culture plates. Similarly, the loss in weight and in physical quality observed by de Vries in moist sheets

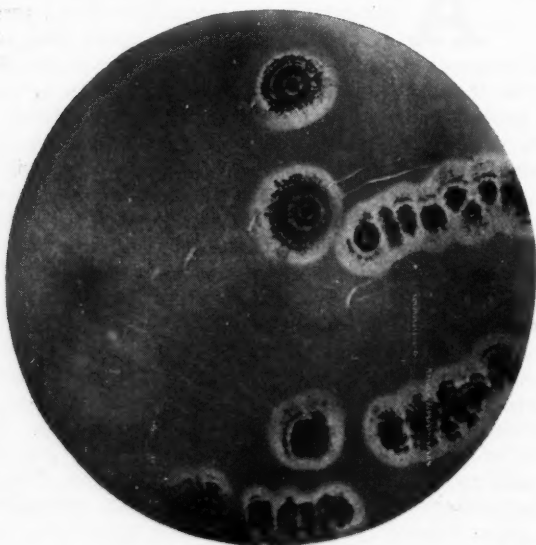


FIGURE 1. ACTINOMYCETES COLONIES ON LATEX-AGAR PLATES

of plantation crepe on which *Penicillium* molds had been allowed to develop was insignificant until after five years of slow development (7).

Sterile Latex

The preparation of a sterile latex suitable for bacteriological study presents a problem in itself, particularly when one has to deal with the product as it arrives in this country preserved with ammonia. However, by dialyzing the latex against a strongly buffered solution, continuously renewed and of about the same pH as fresh *Hevea* latex (6.8–7.2), it is possible to get rid of the ammonia and water-soluble organic crystalloids present in the original latex without coagulation; furthermore, this dialyzed latex can be afterwards sterilized in the ordinary way (15 minutes at 120° C.) without coagula-

tion taking place. Latex, so prepared and sterilized, can be kept apparently indefinitely without coagulation. On standing in the dark some "creaming" occurs in the course of time, but even after six months, gentle shaking of the contents of the flask will bring about a complete redispersion of the globules, provided the latex was properly buffered and sterilized in the first place.

This prepared and sterilized latex was used in the following work. By dilution with sterilized tap water, it is possible to prepare latex dispersions of any given concentration with the requisite amounts of inorganic elements for bacterial growth. Or this latex can be brought to any desired concentration and subsequently resterilized in individual flasks, provided that the pH is maintained unchanged and that ammonium chloride is not added as a source of nitrogen. Even in the small amounts (0.05 per cent) necessary for bacterial growth, this latter reagent brings about coagulation of the latex on sterilization probably because of the decomposition of the ammonium chloride at the temperature of sterilization. Later potassium nitrate was used as a source of nitrogen; it answers every requirement and at the same time overcomes the difficulty described where ammonium chloride is added prior to sterilization.

Working with latex has shown that the decomposition of the rubber hydrocarbon by certain bacteria is both rapid and profound; after a few weeks at 30° C. the greater part of the rubber originally present in the latex has vanished and what is left is a coagulum composed of a mass of bacteria in a residue which has little claim to be called rubber.

Bacteria Strains

So far only those forms of *Actinomyces* derived from garden soil have been used. Four strains prepared in pure culture using agar-latex plates developed for the purpose have yielded characteristic results. When one of them was used to inoculate a prepared and sterile latex, after 4 weeks at 30° C. in the dark, over 70 per cent (by weight) of the rubber hydrocarbon present in the original latex had disappeared. Large colonies of bacteria developed freely and rapidly on the surface and throughout the latex which gradually darkened in color as the decomposition proceeded. After 3 weeks the milky appearance of the latex was gone, and there remained a brownish residue in a clear, brownish, watery serum. This residue turned black on drying and was friable and hard, unlike rubber. After acetone extraction and drying, it contained roughly one-half its weight of bacteria; the remainder was partially soluble in benzene alone and gave a clear, soft, almost oily product on evaporation of the benzene. The product, insoluble in benzene but swelling in it after a time, was readily dissolved in benzene containing trichloroacetic acid and therefore probably represents "insoluble"

rubber. The acetone extract of this product of the latex remaining after bacterial decomposition was over 10 per cent, representing an increase of more than 50 per cent in acetone-solubles compared with the original (sterile) controls. The water liquor from this same latex after bacterial decomposition, when filtered, evaporated to dryness, and incinerated, appeared to contain over 30 per cent by weight of the total coagulum of the original latex in the form of water-soluble organic decomposition products. With barium hydrate a copious white precipitate was formed, although no sulfates had been used in the preparation or coagulation of this latex.

Similar results were obtained with the pure cultures of all four organisms isolated and tested. Marked differences, however, appeared in their rate of development both on the original agar-latex plates and in the latex itself. Although the water-insoluble residue left after bacterial decomposition of the latex was almost black in the case of organisms 1, 2, and 3, and friable or tough but not elastic, in the case of organism 4, there was practically no discoloration in the residue which was still quite white and somewhat elastic. The analytical figures show that the bacterial development in this case was quite as great as that of organism 1. Much less "insoluble" (gel) rubber and also carbon dioxide seem, however, to have been produced in the case of organism 4, indicating a less intensive oxidation of the original hydrocarbon than in the case of the others.

No attempt has yet been made to study the products of decomposition of the hydrocarbon; present efforts were directed towards establishing the fact that the rubber hydrocarbon in latex form can be and actually is readily attacked and almost completely decomposed by bacteria and to the development of practical means to this end. The writers are now in a position to prepare much larger quantities of material than was possible in the first instance and to study the products of decomposition and the course of the reaction in a quantitative way. They are particularly interested in the effect of the addition of an aqueous enzymatic extract of these pure latex cultures upon fresh latex in the absence of the bacteria themselves.

There is every reason to believe that latex fresh from the tree will be much more susceptible to the action of bacteria than the old, ammonia-preserved material. On the practical side, the present results explain the generally poor physical quality of earth and bark scrap rubbers and their blackish color. Early sterilization should provide the remedy. That the physical quality of the rubber hydrocarbon can be profoundly affected by the action of microorganisms applied to the latex is also shown by the marked differences in viscosity here recorded between samples of rubber prepared from latex and from the same material after bacterial infection and development.

Experimental Procedure

The latex used in this work was a 40 per cent product furnished by the U. S. Rubber Company; it contained 1 per cent ammonia. For this work the removal of the ammonia and any water-soluble sugars, etc., from this latex was essential, and the method of dialysis first developed and applied some twenty-eight years ago to the purification of latex (3) and to its analysis (4) was utilized.

Considerable coagulation occurred on the walls of the dialysis tube when the latex was dialyzed against running water, so that it could not be purified in this way without considerable loss of rubber by coagulation. Although this loss was relatively unimportant in these experiments, since it was still possible to obtain a sufficiently concentrated latex for use after dialysis in this way, it was utterly impossible to sterilize the latex without coagulation. This dialyzed latex quickly became foul on standing and finally coagulated of its own accord.

The first series of experiments was carried out with 50 cc. of this dialyzed latex, diluted to 1 liter with tap water and filtered through cheesecloth and subsequently through a No. 1 Schott sintered glass funnel. Four lots of 50 cc. each of this dilute dialyzed latex were measured off, two for immediate coagulation and two for incubation at 30° C. A few drops of toluene were added to the latex in one flask before placement in the incubator and to the other was added a trace of garden soil. The flasks were provided with cotton wool plugs and a few drops of toluene were added to one flask, from time to time, to prevent bacterial growth. The flasks were left in the incubator 6 weeks. The two lots of latex serving as controls were coagulated at once by adding to each of them three drops of 10 per cent sulfuric acid and heating to the boiling point to ensure complete coagulation. The clots formed in each case were filtered, extracted with boiling acetone, kept 6 hours in the dark, and subsequently dried in vacuum over sulfuric acid in the dark until constant in weight. At the end of 6 weeks both lots of latex in the incubator had coagulated more or less completely, but the one containing the soil had turned dark in color and had a powerful, characteristic odor of moist soil. The particles of soil were removed by the centrifuge, and the liquor (with coagulum and washings) was treated with three drops of 10 per cent sulfuric acid and raised to the boiling point. The contents of the other flask containing toluene were similarly treated to ensure uniformity and complete coagulation throughout the series. The clots in each case were extracted with boiling acetone, dried in the dark in vacuum as in the case of the two original controls, and weighed.

In order to effect a complete separation of the bacteria and/or vegetable protein from whatever rubber was still present in the various samples, the method (5) of dissolving the samples in benzene containing 1 per cent trichloroacetic acid was used. In this way it was possible to filter off the bacteria in a sintered glass crucible and, after washing with fresh benzene and drying, to determine the amount in each coagulum. In the case of the control samples, the figures obtained in this way represent the vegetable protein of the rubber.

In addition, and in order to illustrate the difference in quality between the rubber in the control samples and that from the latex in which the bacteria had developed, viscosity determina-

tions were made in dilute solution. A 1 per cent solution in benzene was prepared for this purpose, due allowance being made for the bacteria and protein present in each sample by previous determination. After several weeks of constant shaking in the dark and in the absence of air, the insolubles were allowed to settle out, and the viscosity measurement was made on an aliquot portion of the clear solution which was afterwards evaporated to dryness and weighed. The results of these viscosity measurements confirm the obvious differences in physical quality between the different samples observed by rule-of-thumb tests.

The results obtained by the above methods on the preliminary sample of dialyzed but not sterilized latex subjected to the action of soil bacteria were as follows:

	Latex Coagulated at Once Sample 1	Latex Coagulated at Once Sample 2	Latex after 6 Weeks at 30° C. with: Toluene Soil	
Total dry weight of coagulum, gram	0.4260	0.4260	0.4308	0.3840
Total dry weight of bacteria and/or protein, gram	0.0114	0.0110	0.0112	0.0504
Total residual rubber (by difference), gram	0.4146	0.4150	0.4196	0.3336
Relative viscosity, sec.	20	22	18	3

The coagulum obtained from the soil-treated latex was practically black when dry, and very soft and "dead." All the others were pale and transparent throughout and quite hard and tough. More than 20 per cent of the rubber originally present in this latex was completely decomposed, and that which remained was thoroughly deteriorated, soft, and "dead."

Preparation of Sterile Latex

After months of experimenting on the preparation of a latex which would stand sterilization without coagulation but would contain the inorganic salts and nitrogen necessary to ensure bacterial development, the following satisfactory method was developed. It is capable of wide application where the preservation of latex in general against coagulation in storage or use is desired.¹

The latex is diluted with at least its own volume of a buffer solution made by the addition of the necessary quantity of a 0.05 *M* solution of sodium hydroxide to a 0.05 *M* solution of potassium dihydrogen phosphate in distilled water to bring the pH of the final solution to approximately 6.8 by determination. This latex can now be dialyzed (to get rid of the ammonia and otherwise be purified) into a large volume of this same buffer solution, renewed from

¹ It should now be possible to determine whether the protein of latex can be removed by digestion with trypsin and subsequent dialysis without coagulation. By digestion of sterile latex with active trypsin and subsequent dialysis into a buffer solution of the correct pH, there is some hope of arriving at a decision as to the role of the protein in connection with latex and its coagulation. The conclusions of Freundlich and Hauser [*Kolloid-Z.*, **36**, 21, Zeigmondy Festschrift (1925)] are based on entirely inadequate experimental evidence and are at complete variance with the earlier observations by one of the writers on the effects of trypsin applied both to *Hevea* and *Funtumia latices* (4).

time to time, without any appreciable coagulation. After dialysis in this way and filtration if necessary through a sintered glass filter, this latex can be sterilized by steam for 15 minutes at 120° C. without coagulation, and in this sterile condition can be kept apparently indefinitely, without change. It is necessary only to shake the contents of the flask gently if there is evidence of creaming on long standing, in order to ensure a uniform redispersion of the latex particles. In withdrawing samples for test purposes, it is obviously essential to avoid bacterial contamination from any source. Samples can be taken by sterile pipets and diluted thereafter as required for bacteriological purposes, or the latex after dialysis can be diluted as a whole to any desired concentration by means of tap water containing the necessary salts for bacterial development and then sterilized. The only difficulty experienced is in sterilizing the diluted latex in the presence of ammonium chloride. On the addition of only 0.05 per cent of this material to the diluted latex, coagulation occurs on sterilization. However, the use of potassium nitrate (0.1 per cent) overcame this difficulty. The dialyzed and sterile latex was diluted for the experiments so as to contain, before inoculation, inorganic elements approximately as follows (in per cent): potassium dihydrogen phosphate, 0.1; magnesium sulfate, 0.05; ammonium chloride, 0.05, or potassium nitrate, 0.1, with a rubber content of less than 1 per cent (determined by coagulation tests) and a pH of 6.8 to 7.

In the first experiment carried out with sterile latex prepared in this way, soil particles were again used for inoculation purposes, and the four flasks (two sterile), each containing 100 cc. of latex, were put into the incubator at 30° C. for 35 days. Long before the end of this period the soil-inoculated latex had again darkened in color and completely coagulated; the two sterile controls were still milky white and showed evidence of some agglutination of latex globules but almost no coagulation. The soil particles were removed from the two by centrifuge and all four samples were then treated alike for complete coagulation and analysis as previously outlined. The results of this experiment are shown in the following table and confirm previous findings as far as the effect of soil bacteria on latex is concerned:

	Sterile Latex Controls		Soil-Inoculated Latex	
	No. 1	No. 2	No. 1	No. 2
Final total dry weight of coagulum, gram	0.4786	0.4724	0.4238	0.4308
Dry weight of bacteria and/or protein (by detn.), gram	0.0124	0.0112	0.0648	0.0660
Total residual rubber (by difference), gram	0.4662	0.4612	0.3590	0.3648
Relative viscosity of 1% soln. of benzene-sol. fraction, sec.	14	13	4	3

Here again more than 20 per cent of the rubber originally present in the latex was completely decomposed by the action of the soil bacteria, and the rubber remaining was so deteriorated physically that a 1 per cent solution in benzene had practically the same viscosity as pure benzene (2.75). The residue after benzene extraction in the presence of trichloroacetic acid was a blackish mass which, when ground to powder and examined under the microscope, obviously consisted almost entirely of disintegrated Actinomycetes.

Enrichment of Organisms and Preparation of Pure Cultures from Soil for Latex Decomposition

Washed agar (in water) was used to which the following percentages were added: ammonium sulfate, 0.1; potassium hydrogen phosphate, 0.1; magnesium sulfate, 0.05. The warm agar solution was poured into Petri dishes and allowed to cool and harden, then covered with a thin layer of a milky white suspension of sterile latex in water-agar medium, and inoculated with soil particles. Incubation was carried out at 20°, 25°, 30°, and 37° C. Colonies, chiefly Actinomycetes, quickly appeared on all plates and developed most rapidly at 25° to 30° C. Pure cultures of four distinct strains were prepared by four repeated replatings on the same medium. All four strains showed more or less distinct clear zones in the opaque latex-agar medium surrounding the individual colonies. (Figure 1 shows a photograph made by transmitted light.) Whether this is due to extracellular enzymatic decomposition of the latex or not remains to be determined.

Preparation of Latex for Inoculation with Pure Cultures

For this series a dialyzed latex was used and diluted with standard 0.05 *M* buffer solution to bring the rubber concentration to approximately 5 per cent. Eleven flasks, each containing a solution of 0.1 per cent potassium nitrate, 0.1 potassium hydrogen phosphate, 0.05 magnesium sulfate, and brought to a pH of 7.0 by means of potassium dihydrogen phosphate, were prepared; to each were added 5 cc. of the latex. All eleven flasks were successfully sterilized for 20 minutes at 120° C. without any coagulation. Two of these flasks of sterile latex were immediately coagulated, and the rubber content was determined. Two other flasks were set aside to be placed in the incubator with the remaining seven which were inoculated as follows: two with strain 1, two with strain 2, one with strain 3, and two with strain 4. All nine flasks were left in the incubator at 30° C. for 28 days.

In a week, bacterial growth was clearly evident, particularly in the case of strains 1 and 3. In 3 weeks, all milkiness had disappeared, and instead large colonies had developed on the surface and throughout the liquors. The colonies were smaller in the case of strain 2. Contents of 1, 2, and 3 had turned dark. After 4 weeks strain 4 alone appeared as white moldlike colonies in a clear liquor; the others were now almost black. All had the characteristic odor of moist soil. The sterile controls after 4 weeks in the incubator came out slightly coagulated, but were still milky and apparently unchanged.

The control samples of latex from the incubator and one of each of the samples containing the various strains were

TABLE I. RESULTS OF EXPERIMENTS

Total dry weight of coagulum, gram Appearance of coagulum	Sterile Latex Controls Coagulated at once—				Latex after 28 Days at 30° C. with:			
	Coagulated at once—		Coagulated after 28 days at 30° C.		Strain 1		Strain 2	
	1	2	1	2	Strain 1	Strain 2	Strain 3	Strain 4
Dry weight of bacteria and/or protein in coagulum, gram	0.248	0.246	0.245	0.243	0.144	0.195	0.1494	0.1046
Total rubber (benzene and acid sol.), by difference, gram	0.0079	0.0076	0.0083	0.0083	0.0704	0.0378	0.0426	0.0760
Benzene-sol. rubber only, gram	0.2401	0.2384	0.2367	0.2347	0.0736	0.1572	0.1068	0.1186
Not determined	Not determined	Not determined	Not determined	Not determined	0.0475, very soft and plastic	Not determined	Not determined	0.1062, soft and plastic
Original rubber lost, %	70	36	56	51
Water sol. in serum (loss by dialysis), gram	0.0856	0.0651	0.0316
Acetone-sol. extract, gram (%)	0.0074 (3.0)	0.0070 (2.88)	0.0156 (10.8)	0.0124 (6.4)	0.0160 (6.2)	0.0170 (8.7)

* The actual losses are undoubtedly higher because the residues left were oxidized rubber, to a greater or less extent.

treated alike with five drops of 10 per cent sulfuric acid and raised to the boiling point. The clear liquor was filtered off, and the residue or coagulum well washed with boiling water, finally extracted with boiling acetone in the dark, and dried in vacuum in the dark until constant in weight. In this series the acetone extracts were also evaporated to dryness and weight. The benzene-soluble content was determined in samples of the residues from strains 1 and 4 only while the bacteria, together with any protein still present, were separated by the benzene-trichloroacetic acid method in each case and weighed. In this way the amount of benzene-insoluble rubber present in strains 1 and 4 was estimated. The water liquors from the additional flasks containing strains 1, 2, and 4 were used to determine the organic matter present in these liquors at the end of the incubation period. The bacteria and water-insolubles were filtered. The residual liquors were boiled, refiltered, and finally evaporated to dryness and weighed before and after ignition in a platinum crucible. Extensive charring occurred with strain 1, very little with strain 4. This same liquor from strain 1 gave a copious precipitate on addition of barium hydroxide, strain 2 very much less, and strain 4 only a trace. Insufficient material prevented further investigation. The results of this series are given in Table I.

It is clearly evident that the rubber hydrocarbon in the latex of *Hevea* is readily attacked by microorganisms of aerobic type and ultimately decomposed into products with very little physical resemblance to India rubber. That such agencies may exert a profound influence on the final quality of the rubber prepared from various latices and may help to explain the still unsolved problem of plantation rubber variation is clearly indicated from the preliminary results.

The preparation of a sterile latex from *Hevea* opens up ways and means for a complete investigation of this whole subject as a practical problem of the utmost importance to plantation owners and rubber manufacturers alike; also the foundation has been laid for a study of the reactions and products involved in the building up and breaking down of the rubber hydrocarbon by the living plant.

Acknowledgment

The writers wish to express their thanks to W. A. Gibbons and H. L. Fisher of the U. S. Rubber Company for their assistance in furnishing the latex used in this work. They also desire to thank H. Albert Barker for many valuable suggestions made in the course of this work and also A. W. Martin for preparing the photograph illustrating the characteristic appearance of *Actinomycetes* development on latex-agar plates.

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A New Rubber Particle Count in Hevea Latex

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SO MUCH confusion has grown up in the literature concerning the number of rubber particles in Hevea latex that at the present time there exists a thousandfold error in the currently published reports (1, 3, 8) of the one original determination of this number. Harries (4), Hauser (5), and Noble (8), each reporting the original work of Henri (6), give a count of 50,000,000 particles per cubic centimeter of latex, Harries not specifying the concentration, while Hauser and Noble indicate it to have been 8.7 per cent solids. On the other hand, Dubosc and Luttringer (2), also reporting the work of Henri, record a count of 50,000,000 particles per cubic millimeter in latex of unspecified concentration. The original paper of Henri (6) reported that he had found an average of 50,000,000 particles per cubic millimeter of latex having a specific gravity of 0.973 and containing 8.7 grams of solids per 100 cc. Preliminary counts undertaken by the author with a view to developing a rapid microscopic method for the determination of the dry rubber content of latex indicated that the results of Henri were considerably low. Since the number of microscopically visible particles is a fundamental property of latex, it was felt that a redetermination of this number would be of value.

Experimental Method

PREPARATION OF SOLUTIONS. From 1.0 to 2.0 grams of ammonia-preserved 38 to 40 per cent latex, the solids and dry rubber content of which had been determined, were weighed by difference, using a medicine dropper, into a 1-liter volumetric flask nearly filled with water to which had been added 15 ml. of 26° Bé. ammonium hydroxide solution to prevent any tendency to flocculation of the latex. The mixture was made up to volume and, after careful shaking, 20 ml. were pipetted out into a 500-ml. volumetric flask almost filled with a filtered 20 per cent sodium chloride solution. The sodium chloride solution was used to stop the Brownian movement of the rubber particles which would render the counting difficult. After being made up to volume with the same salt solution, the necessary amount of the solution, which represents a dilution of the original weight of latex to 25,000 ml., was transferred to the counting chamber using, for convenience, a Thoma blood-diluting pipet.

COUNTING CHAMBER. A Levy counting chamber with the improved Neubauer ruling (9), such as is used in counting blood corpuscles, was used in this work. The counting cell consists essentially of a plane surface of glass containing a

centrally located square 1 mm. on a side. This central square millimeter is ruled into 400 equal squares. By means of double marginal rulings these 400 smallest squares are grouped into 25 squares, each containing 16 small squares representing an area of 0.04 sq. mm. Facilities are provided for supporting an optically plane cover glass 0.1 mm. above and parallel with this ruled surface, thus forming a chamber of 0.1 cu. mm. capacity. The volumetric accuracy of the counting chamber is of the order of 4 per cent. One group of 16 of the smallest squares is visible simultaneously with a 4-mm. objective and a 10 \times Huygenian ocular.

THE MICROSCOPE. A Hartnack and Prasmowski microscope was used. A No. 7 objective, with corrective lens for cover glass thickness, and a No. 3 eyepiece were used in making the counts. This combination of lenses represents a magnification of about 400 diameters. Since no mechanically operated stage was available, it was necessary to provide otherwise for the orderly movement of the counting chamber. This was accomplished by daubing a small quantity of a mixture of 70 per cent rosin and 30 per cent rapeseed oil onto each end of the under surface of the counting chamber, which, by its viscous drag, prevented the capricious movement of the counting chamber when touched by the hand to bring a new group of squares into view. Because the counting chamber depth was great in comparison to the depth of focus of the objective used, it was necessary to focus slowly upwards from the ruled surface of the counting cell to the lower surface of the cover glass in counting each small square in order to assure the inclusion of all the particles. To prevent duplication, the particles were counted only when they came into sharp focus. It was noticed that because the Brownian movement had been stopped there was a pronounced tendency for the particles to settle upwards towards the cover glass and that after the counting chamber had been filled for about 10 minutes fully 75 per cent of all the particles were found in the focal plane nearest the cover glass. Since the boundary lines were least distinct in this focal plane, it was necessary to refill the cell frequently.

THE LATEX. The samples of latex used were obtained from drums of commercial 38 to 40 per cent ammonia-preserved latex. Two of these samples were of the brand known as "No. 4 Plantation Latex," marketed by the Vultex Chemical Company, Cambridge, Mass., and one sample of the brand "Lotol," marketed by the Naugatuck Chemical Company, Naugatuck, Conn.

Results of Counts

The results of the several counts on the different latex samples appear in Table I. The number of particles per gram of latex is the value reported, and for the purpose of comparison among the several samples of latex, which varied

slightly in dry rubber content, all the counts are corrected to a common basis of 35 per cent dry rubber content.

TABLE I. RESULTS OF COUNTS

Brand of Latex	Sample No.	Dry Solids %	Dry Rubber Content %	Groups Counted ^a	Particles per Gram ^b
No. 4 Plantation	1	38.4	35.3	2	0.62×10^{12}
	1	38.4	35.3	3	0.65×10^{12}
	1	38.4	35.3	1	0.62×10^{12}
	2	38.5	34.6	4	0.63×10^{12}
	2	38.5	34.6	3	0.60×10^{12}
Lotol	3	39.0	35.9	1	0.64×10^{12}
	3	39.0	35.9	3	0.69×10^{12}

^a Group of 16 small squares.

^b Corrected to 35 per cent dry rubber content.

An average of all the counts recorded in Table I, weighted on the basis of the number of groups counted, gives a figure of 640,000,000,000 rubber particles per gram of latex of 35 per cent dry rubber content. The count of Henri, calculated to the same basis, using the factor 0.92 for conversion from per cent solids to dry rubber content, gives a figure of 218,000,000,000 particles.

Discussion of Results

It must be realized that because there is known to be numerically considerable material of ultramicroscopic proportions in latex which cannot be included in any such particle count as is reported here, but which does contribute slightly to the rubber content of the latex, such a count is inevitably low. If, however, we are willing to neglect the contribution of the ultramicroscopic material to the rubber content of the latex, it is possible to calculate an average particle diameter. In making such a calculation based on the count reported here spherical shape has been assumed for the particles, and a density of 0.914 for the material of the particles⁸ was used. On this basis the average rubber particle size in the latex samples used in this investigation is 1.04 microns. The average diameter of the rubber particles of Hevea latex has been determined by Wightman and Trivelli (10), using motion photomicrographs, to be between 0.7 and 0.8 micron. On the other hand, Madge (7) states that "the particles of commercial latex have on an average a diameter of approximately 1.5 microns as measured with a microscope."

Acknowledgment

The author's grateful thanks are due to the Union Paste Company of Medford, Mass., whose facilities and materials were graciously extended for the conduct of this investigation, and to Purcell G. Schube, Boston State Hospital, Boston, Mass., not only for the use of the blood-counting apparatus, but for much helpful advice and many suggestions.

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Determination of Sulfur in Rubber Compounds

I. Precipitation of Barium Sulfate in the Presence of Picric Acid

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THERE is probably no single operation in analytical chemistry that has received more attention from investigators than that of precipitation of barium sulfate by means of a soluble barium salt for the determination of sulfate or of barium. The literature on this subject is voluminous and the conclusions reached by different investigators as to the proper procedure to employ in order to obtain a precipitate which will be filterable and reasonably pure are highly contradictory. The procedure which seems to be in most general use at present for the determination of sulfate is that of adding the barium chloride solution to the hot sulfate solution very slowly, stirring vigorously meanwhile, then allowing the whole to digest at an elevated temperature for several hours before filtering.

The diversity of opinion as to the proper procedure arises, the author believes, from the fact that the barium sulfate precipitate is exceedingly sensitive to its environment and that a very slight change in the amount or kind of impurities present in the solutions during precipitation has a profound effect upon the crystal size and shape of the precipitated particles as well as upon their purity. Kolthoff and Vogelenzang (2) have stated that it is impossible to prescribe a general procedure for the accurate precipitation of sulfate in arbitrary mixtures. In other words, a precipitation procedure which gives satisfactory results in the determination of sulfur in copper ores, for instance, may not yield a satisfactory precipitate when applied to the determination of total sulfur in hard rubber dust, and a study of each type of determination, with due consideration for the amount and kind of impurities present, must be made in order to find the conditions necessary to obtain a precipitate which is pure and easily filterable.

For several years it has been known to a few analysts that the presence of picric acid in the sulfate solution at the time of precipitation would yield a precipitate which could be filtered immediately without the necessity of prolonged digestion before filtration. This bit of information has not appeared in the literature, although Dubrisay and Toquet (1) in 1919 suggested the use of phenol; and at present picric acid is being used in a number of laboratories throughout the country. Thus, the author does not claim in any sense that

the use of picric acid is original with him, but presents this study in the hope that its use will become as widespread as it deserves.

The technic employed in the use of picric acid is simple. From 1 to 5 cc. of a saturated solution of picric acid in water are added to the acidified sulfate solution and stirred in before adding the barium chloride. The barium chloride may be added quickly, as nothing is gained by adding it slowly. After adding the barium chloride (which should be in excess as small as practicable) the solution should be gently boiled for from 5 to 10 minutes. It will then be ready to filter. In case the sulfate solution contains large quantities of sodium salts, as in sulfur determinations on Parr peroxide bomb residues, or strong oxidizing acids, as in the perchloric acid method for total sulfur in rubber compounds, the amount of picric acid necessary to produce the desired effect may be greater than that given above and in these cases from 10 to 25 cc. of the saturated solution should be used.

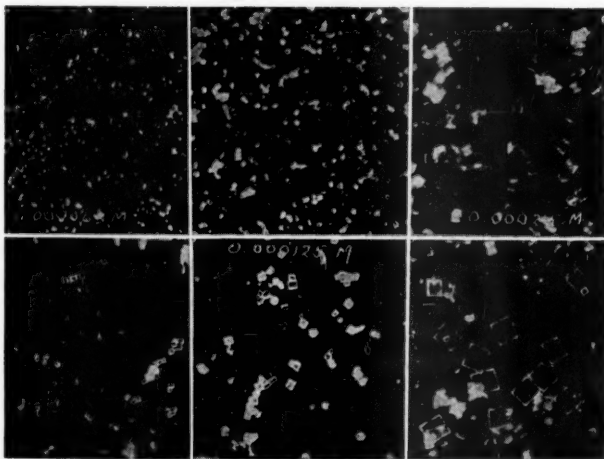


FIGURE 1

In the company's laboratories, picric acid has been in constant use for the past 8 years in the determination of free sulfur in rubber compounds by the bromine-oxidation method and of total sulfur by oxidation with perchloric acid. It has been known all this time that its use greatly improved the filterability of the precipitated barium sulfate without deleterious effect on the quantitative results, but no systematic study of the phenomenon was made until within the last few months.

When the use of picric acid was first under consideration, a long series of parallel determinations showed that the quantitative results obtained with and without picric acid were, if not identical, at least within the limits of accuracy of the methods of analysis themselves. These observations have been confirmed in the recent study, as shown in Table I, which gives the results obtained using pure solutions of sulfuric acid as the source of sulfate ions. In each case, the numerical re-

sult given is the average obtained from determinations run in triplicate.

TABLE I. PRECIPITATION OF BARIUM SULFATE

No.	Water Cc.	0.1 N H ₂ SO ₄ Cc.	Picric Acid Cc.	10% BaCl ₂ Cc.	Bromine Cc.	BaSO ₄ Gram
1	100	20	0	15	0	0.2333
2	100	20	1	15	0	0.2359
3	100	20	0	15	3	0.2337
4	100	20	1	15	3	0.2364
5	400	20	0	15	0	0.2355
6	400	20	1	15	0	0.2358
7	250	4	0	10	3	0.0457
8	250	4	1	10	3	0.0464
9	400	1	0	1	0	0.0105
10	400	1	1	1	0	0.0105

In each case, the result obtained where picric acid is present is slightly higher than where it is absent. When the gravimetric factor for converting barium sulfate to sulfur

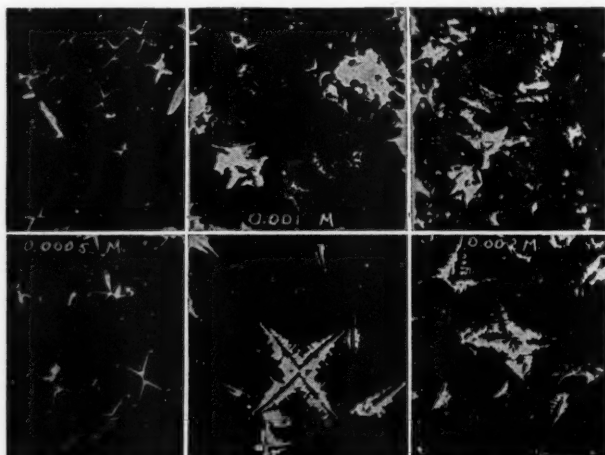


FIGURE 2

(0.13136) is applied to this difference, it is divided by approximately 7.3 and becomes smaller than the usual difference between duplicate determinations, although it is always positive in sign. These results removed any fear that picric acid might increase the solubility of barium sulfate and cause incomplete precipitation.

Runs 3 and 4 differ from 1 and 2 in the fact that before the barium chloride was added 3 cc. of bromine were added, allowed to stand for 30 minutes, and then boiled off, after which the picric acid was added and the precipitation performed as usual. This was done to determine whether bromine or hydrobromic acid would have any appreciable effect upon the result, which is apparently not the case. Runs 7 and 8 are in approximately the range of concentration which is encountered in free sulfur determinations on nonblooming tire stocks. Runs 9 and 10 are very dilute, and the excess

of barium chloride is low in concentration. The exact agreement obtained in these last runs would make it appear that the differences in results obtained in the previous runs were due to increased occlusion or adsorption of barium chloride brought about in the presence of picric acid. The results given in Table II show that this probably is the case.

TABLE II. PRECIPITATION OF BARIUM SULFATE

No.	Water Cc.	0.1 N H ₂ SO ₄ Cc.	Picric Acid Cc.	0.5 N BaCl ₂ Cc.	BaSO ₄ Gram
1	250	25	0	20	0.1163
2	250	25	1	20	0.1161
3	100	20	0	15	0.0870
4	100	20	1	15	0.0873

In these runs, the barium chloride present was insufficient to react with all the sulfuric acid present, so that there was no excess, but rather a deficiency of barium chloride. The re-

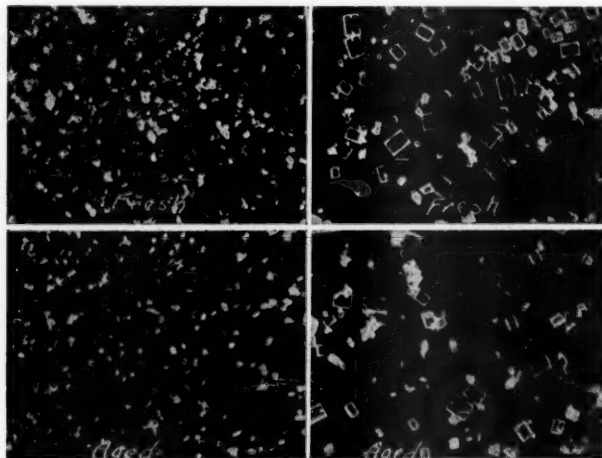


FIGURE 3

sults are well within the limits of accuracy of the ordinary volumetric buret and the differences are opposite in sign in the two pairs of runs, which differ considerably in concentration, runs 3 and 4 being twice as concentrated as runs 1 and 2.

Since we now have very good evidence that picric acid increases the adsorption of barium chloride by barium sulfate, to a very small extent, it was logical to believe that it might have a similar effect upon other ions which might be present as impurities in the solution. Since iron is commonly present in solutions from which barium sulfate is precipitated, a pair of runs was made in which ferric chloride was present. After filtering the precipitates obtained, they were analyzed

and the iron was determined. The results are shown in Table III.

TABLE III. DETERMINATION OF IRON

No.	Water Cc.	0.1 <i>N</i> H ₂ SO ₄ Cc.	1% Picric Acid Cc.	10% BaCl Cc.	15% FeCl ₃ Cc.	Fe in BaSO ₄ Gram
1	250	25	0	10	2	0.057
2	250	25	5	10	2	0.0051
3	250	25	0	10	2	Faint trace
4	250	25	5	10	2	Faint trace

In runs 1 and 2 an appreciable amount of iron was picked up. It had been foreseen that iron might be adsorbed by the filter paper, so extraordinary precautions were taken in washing. The filters were washed at least 30 times with boiling water and the washings tested colorimetrically for iron. In the last 5 or 6 washings no iron was detectable, yet the appearance of the ignited barium sulfate led to the belief that the filter paper itself was responsible for a considerable portion of the total iron present. Accordingly, runs 3 and 4 were made, using fritted glass filters instead of paper for the final filtration. The precipitate was then removed from the filter and analyzed for iron as before. This time, the colorimetric test for iron was so faint as entirely to prevent its quantitative estimation.

Table IV shows the results obtained in actual free sulfur and total sulfur determinations. These figures are typical of those obtained from hundreds of comparison determinations made during the last 8 years.

TABLE IV. RESULTS IN ACTUAL SULFUR DETERMINATIONS

Sample	Sulfur without Picric Acid %	Sulfur with Picric Acid %
156A (free sulfur)	0.35	0.37
	0.35	0.37
159	0.40	0.40
	0.40	0.40
160	0.32	0.33
	0.32	0.33
1 (total sulfur)	1.944	1.946
2	2.561	2.562

That the effectiveness of picric acid in increasing the ease of filtration is due to an actual increase in particle size of the barium sulfate crystals and not to any coagulating effect of the reagent is illustrated in the accompanying photomicrographs.

Figures 1 and 2 show the crystals obtained from sulfuric acid solutions of various concentrations. In Figure 1, upper row, the concentrations were 0.000063 *M*, 0.000125 *M*, and 0.00025 *M*, respectively, reading from left to right. The lower row shows the precipitates obtained from solutions of the same concentrations, containing in addition 0.0025 per

cent of picric acid. The precipitates in the first two photographs, top row, were not entirely held up by a Carl Schleicher Schull 589 Blue Ribbon filter, while all the precipitates formed in the presence of picric acid were held up completely by this grade of paper. In Figure 2, the concentrations of the solutions were 0.00050 *M*, 0.001 *M*, and 0.002 *M*, respectively, the lower row containing the same amount of picric acid as in Figure 1. In all these experiments, the precipitates prepared

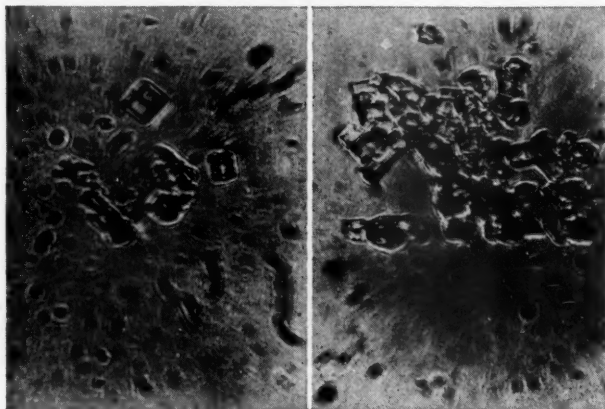


FIGURE 4

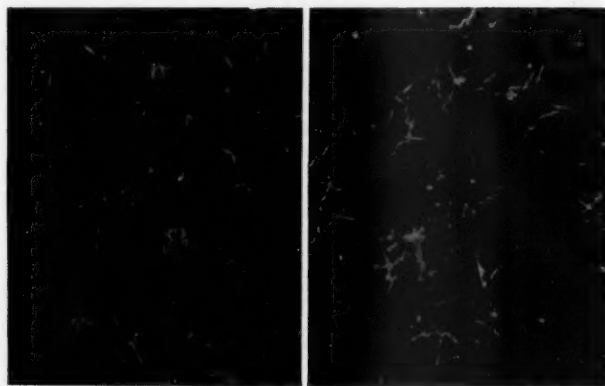


FIGURE 5

without picric acid were digested at 80° C. for 16 hours before photographing, while those prepared with picric acid were photographed immediately after precipitation.

In this connection it was interesting to note that digestion of the barium sulfate for 16 hours at a temperature of 80° C. had no significant effect upon the particle size. In no case could any change in particle size be detected until the diges-

tion had progressed for several days. There is a generally accepted belief that during digestion the smaller crystals tend to pass into solution, while the larger crystals grow still larger at the expense of the smaller ones. There is no doubt that this process will take place if sufficient time be given, but it

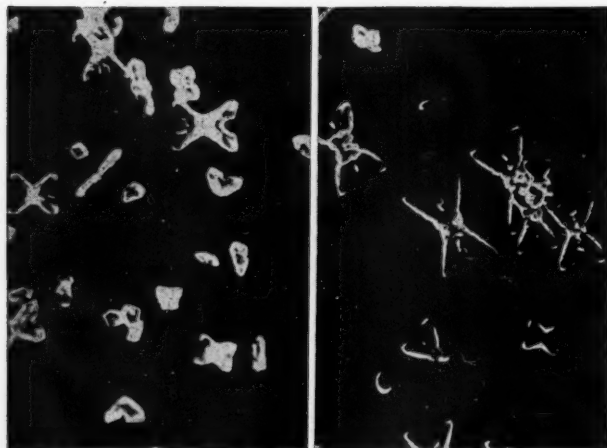


FIGURE 6

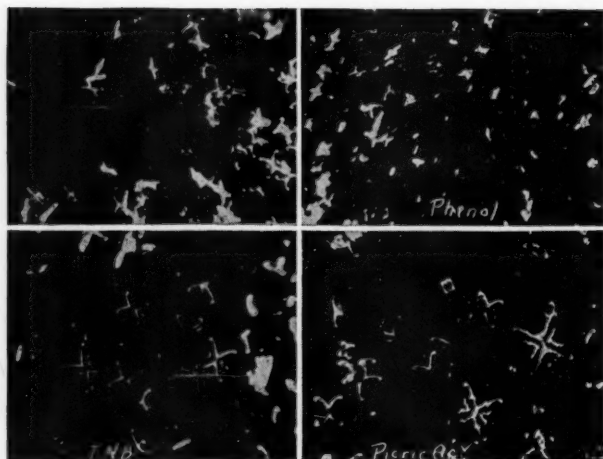


FIGURE 7

is much too slow to have any appreciable effect during the usual overnight digestion.

Figure 3 shows the appearance of fresh precipitates, without and with picric acid (top row), and the same precipitates after 16 hours' digestion (bottom row). There is no perceptible difference in the crystal size of the fresh and aged precipi-

tates. Since there can be no doubt that overnight digestion does improve the filterability of barium sulfate, some other process must take place and a further investigation showed that there occurred a cementation of the individual particles into larger groups or aggregates as shown in Figure 4. On the left is shown the fresh precipitate and on the right the same precipitate after 16 hours' digestion, special precautions having been taken to prevent the breaking up of the rather loosely cemented aggregates in mounting them on the microscope slide. This process of aggregation has also been observed by other investigators, notably Trimble (3) of the University of Oklahoma.

Figure 5 shows the appearance of the precipitates obtained in a regular free sulfur determination by the bromine-oxidation method, without and with picric acid, respectively. In Figure 6 are shown the precipitates obtained in the determination of total sulfur by oxidation with perchloric acid. Figure 7 shows the effect of materials other than picric acid. The upper left photograph shows the crystals obtained from pure sulfuric acid and barium chloride solutions; those in the upper right were precipitated in the presence of approximately 0.5 per cent of phenol; those in the lower left were precipitated from a saturated solution of trinitrobenzene; while those in the lower right were precipitated in the presence of 0.0025 per cent of picric acid. In the presence of phenol, the crystals are actually decreased in size. Trinitrobenzene increases the particle size to some extent, but its low solubility in the aqueous solution probably prevents its being as effective as picric acid.

It has been the author's experience that, in every case, the particle size of the barium sulfate precipitates has been materially increased by the presence of picric acid. It is not recommended in any sense as a cure-all for filtration troubles with barium sulfate, but its use will save a great deal of time and trouble if properly applied to the particular type of sulfur determination in question.

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(Part II follows)

II. Sources of Error in the Determination of Free Sulfur in Rubber Compounds Containing Rapid Accelerators and Sulfur Bearing Accelerators

IT HAS been known for many years that the classic analytical methods for determining the degree of vulcanization of rubber stocks—namely, determination of the combined sulfur directly on an acetone-extracted sample, or indirectly by determining the free sulfur and subtracting it from the total sulfur—possessed certain inherent errors. In the older types of stocks, using relatively slow accelerators, those errors were either too small to be disturbing or could be compensated for by fairly simple calculations, taking into consideration the amounts of sulfur-bearing ingredients such as lithopone, barytes, rubber substitute, mineral rubber, etc., known to be in the stock. Furthermore, the physical properties of the stocks had been cataloged in the minds of the compounders by long experience, as fairly simple functions of the temperature and time of cure. Hence, little attention was paid to these errors in sulfur determinations, and the compounder could obtain a fairly good mental picture of the state of cure from the total sulfur and free sulfur results furnished him by the laboratory.

Of late, however, the picture has been changed by the introduction and widespread use of sulfur-bearing accelerators and of accelerators of the "ultra" and "semi-ultra" type. The compounder has found that he must accustom himself to physical properties which no longer vary as simple functions of the temperature and time of cure, and the analyst finds that the free sulfur which he still tries to determine by the bromine-oxidation method is no longer simply elemental sulfur which failed to react with rubber during the vulcanization process, but may be in the form of a number of other things enormously more complicated. Furthermore, he may find that extraction with acetone—the foundation upon which his free sulfur determination rests—is not the clean-cut solvent operation that it was in the days before the more rapid accelerators came into common use.

The American Society for Testing Materials defines "free sulfur" as "that which is removed during acetone extraction" (1). No explanation is given as to whether this definition shall be construed to mean all sulfur extracted by acetone or only the elemental sulfur.

Free sulfur determinations on stocks containing rapid accelerators or sulfur-bearing accelerators are subject to the following errors:

1. Elemental sulfur introduced into the compound as an impurity in the accelerator
2. Sulfur in the molecule of the accelerator
3. Sulfur in the acetone-soluble products of the vulcanization reaction

4. Sulfur in acetone-insoluble combinations other than with rubber
5. Curing of the stock during extraction with acetone

These sources of error are, of course, in addition to the sources of error found in the older types of compounds—namely, combination of a part of the elemental sulfur with resins and with various fillers to form sulfides, introduction of sulfur into the stock in fillers such as barytes, rubber substitute, etc.

The first source of error—elemental sulfur occurring in the accelerator as an impurity—is probably the smallest and least disturbing of all. The commercial sulfur-bearing accelerators may contain 6 per cent or even more of elemental sulfur, but its net effect is simply a change in the total elemental sulfur as shown in the recipe. Because of the small amounts of accelerator usually used, this change is small.

TABLE I. DETERMINATION OF SULFUR

Cure, at 25 pounds (130.4° C.), min.	Raw	30	45	60	240
Free sulfur, bromine method, %	0.82	0.37	0.30	0.29	0.21
Elemental sulfur, %	0.50	0.128	0.046	0.059	0.045
Difference, %	0.32	0.242	0.254	0.231	0.165
MBT in acetone extract, %	2.91	2.28	1.95	1.80	1.64

Items 2, 3, and 4—sulfur in the accelerator molecule, sulfur in the acetone-soluble, and in the non-acetone-soluble products of the vulcanization reaction—are closely related and may be considered together. For simplicity in explanation, let us see the effect of these three sources of error on the results of sulfur determinations on stocks containing a specific accelerator—mercaptobenzothiazole (MBT). This material contains two atoms of sulfur in the molecule: a mercapto sulfur or —SH group and a ring sulfur in the thiazo group.

Upon treatment with bromine, as in the bromine-oxidation method for free sulfur, the mercapto sulfur is readily oxidized and appears in the result. The ring sulfur is not appreciably oxidized and is lost unless a more drastic oxidizing agent such as perchloric acid is used. Thus, of whatever unchanged mercaptobenzothiazole in the cured stock goes into the acetone extract, approximately half of its sulfur (the mercapto sulfur) appears in the result. The amount of unchanged mercaptobenzothiazole present in a cured stock is a function of various factors, such as time of cure, composition of the stock, etc., and so long as any unchanged mercaptobenzothiazole is present which can go into the acetone extract (and it is probably always present, no matter how long the cure) there is a positive error in determining the extracted sulfur. This error is dependent, among other things, on (1) mercaptobenzothiazole-sulfur ratio in the recipe—that is, the lower the proportion of sulfur, the greater will be the error—and (2) the extent of the cure, which progressively removes a part of the mercaptobenzothiazole as a source of sulfur available for oxidation with bromine.

It is possible that the mercaptobenzothiazole-sulfur ratios

at various stages of a cure can be such that the acetone-extractable sulfur due to the accelerator may be several times greater than the actual amount of elemental sulfur. Table I, illustrating such a condition, shows results obtained from a stock containing rubber 100, zinc oxide 5, stearic acid 1, MBT 3, and sulfur 0.5 parts.

The elemental sulfur was determined on the stock by the method of Guppy (2), which does not appreciably decompose

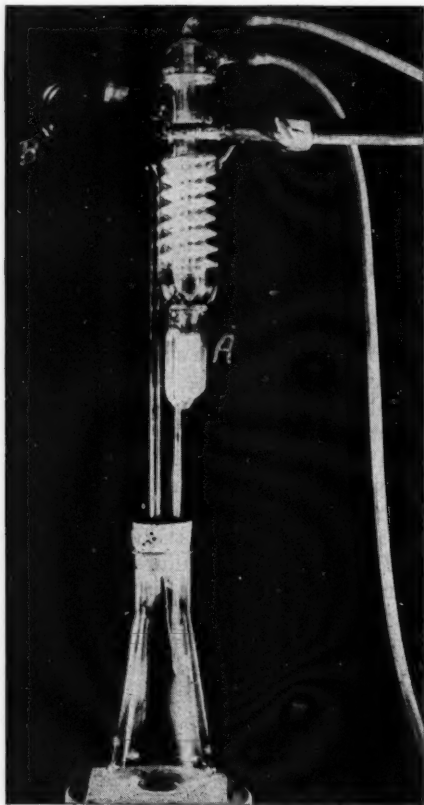


FIGURE 1

mercaptobenzothiazole in the short time required for the determination, while the mercaptobenzothiazole determinations were made by precipitation of its copper salt from benzene solution by means of copper oleate.

From these results it is obvious that the error due to mercapto sulfur is by no means constant. The numerical error is progressively smaller but proportionally larger as the cure increases and the extractable mercaptobenzothiazole decreases. With such proportions of curing ingredients, it is of such

magnitude as seriously to affect the result, especially in long overcures. In the cures above 30 minutes, the elemental sulfur has practically disappeared, yet the "free sulfur" is still appreciable.

Regarding the sulfur compounds present in the acetone-soluble products and in the acetone-insoluble products of the vulcanization, very little is known except that they exist. It is not unlikely that during the cure, the mercapto group splits off from some of the mercaptobenzothiazole, leaving the benzothiazole group either combined with other substances, split up in various ways or in the form of metallic complexes. Some of these reaction products may be readily soluble in acetone, others very difficultly soluble, and removed only by very prolonged extraction, while still others are not removed by acetone at all. These last, unless removed by some solvent other than acetone, remain in the extracted sample, later to appear as "combined" sulfur upon oxidation with perchloric acid.

The last item of error—cure during the extraction with acetone—is probably the largest of all, and is certainly the most disturbing, since it eliminates at one stroke all analytical methods which depend upon the accepted methods of acetone extraction. The extraction maintains the sample at a temperature of 57° C. (135° F.) and many accelerators cure noticeably at this temperature, while some may even be activated somewhat by the acetone. An indication of the significance of this phenomenon will be seen in Table II, which shows the results obtained by the regular extraction and bromine-oxidation method and by Guppy's method on a stock containing rubber 100, zinc oxide 5, stearic acid 1, MBT 0.5, and sulfur 3 parts.

TABLE II. COMPARATIVE RESULTS

Cure, at 25 pounds (130.4° C.), min.	Raw	30	45	60	240
Free sulfur by extraction and bromine oxidation, %	2.37	0.73	0.37	0.20	0.06
Elemental sulfur by Guppy's method, %	2.42	0.85	0.44	0.29	0.06

Here, it will be seen that the elemental sulfur result is higher than the "bromine free sulfur" result, even though the bromine oxidation gives the elemental sulfur plus the mercapto sulfur in the acetone extract. In other words, sufficient cure has taken place in the process of extraction to make the bromine free sulfur appear lower than the elemental sulfur, in spite of the positive error due to the mercapto sulfur.

Various methods have been tried to prevent, or at least reduce, the magnitude of this cure during extraction and the most effective method so far developed has been that of cold extraction—that is, by using an apparatus in which the acetone is cooled to or below room temperature before coming in contact with the sample. The apparatus used was one built

up of glassware available in most laboratories and is shown in Figure 1.

The sample is placed in the siphon cup, *A*, which is an ordinary Pyrex cup having an extension sealed to the lower end of the siphon, so as to give it sufficient length to pass through a cork stopper which is placed in the regular A. S. T. M. extraction flask. The vapor tube, *B*, carries the acetone vapors from the flask to the top of a Friedrich condenser, through which the condensed vapors pass, cooling the acetone to approximately tap-water temperature before it comes in contact with the sample. The top of the siphon cup is in loose contact with the bottom of the condenser, thus keeping evaporation at a minimum and at the same time allowing sufficient venting for the apparatus. The sample is extracted on this apparatus for 16 hours and then is transferred to a regular A. S. T. M. siphon cup, and the flask with its contents is removed from the stopper and placed on the customary hot plate where the extraction is continued, hot, until complete. Thus the first stage removes a large portion of the curing ingredients without heating the sample to a curing temperature, and the process is finished at the higher temperature to insure complete extraction.

In Table III is shown the effect of such an extraction upon the combined sulfur.

TABLE III. EFFECT OF COLD EXTRACTION

Stock	Z-516	Z-517
Rubber	100	100
Zinc oxide	5	5
Stearic acid	1	1
MBT	0.5	3
Sulfur	3	0.5
Total sulfur, elemental and in MBT, calculated, %	2.914	1.505
Combined sulfur, left by hot extraction of raw stock, %	1.09	0.44
Combined sulfur, left by cold extraction of raw stock, %	0.05	0.19

Thus, with the present bromine method the "free sulfur" determined is actually the elemental sulfur plus a more or less indefinite fraction of the sulfur in the accelerator molecule and minus the sulfur lost in cure during extraction. Therefore, the definition given for free sulfur and the method given for its determination are incompatible, and until the definition is changed to remove its ambiguity and the method changed to fit the revised definition, the rubber analyst is left in a rather embarrassing position with regard to this very important determination.

Literature Cited

- (1) A. S. T. M. Standards, p. 1135 (1933).
- (2) Guppy, W. D., *Rubber Chem. Tech.*, 5, 360-2 (1932).

Determination of Guanidines in Rubber Stocks and Consumption of Guanidines during Cure

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QUANTITATIVE determinations of various accelerators that may be present in vulcanized rubber stocks are necessary, not only for fundamental investigations into the mechanism of acceleration, but also for routine control analyses and the examination of unknown stocks. The determination of any organic material in vulcanized rubber stocks is beset with numerous difficulties, however, and reliable methods are scarce. For accelerators, the only ones described in the literature are the now generally employed copper oleate method for mercaptobenzothiazole and an extension of Callan and Strafford's (1) picric acid method for guanidines, both described by Wistinghausen (2). Using these two procedures, Wistinghausen made an extended investigation of the consumption of mercaptobenzothiazole and of diphenylguanidine (D. P. G.) during cure.

Considerable difficulty was encountered in this laboratory in the use of Wistinghausen's method. Especially with di-*o*-tolylguanidine (D. O. T. G.) stocks, the results were highly variable and the proportion of guanidine recovered seemed to be much smaller than that recovered by Wistinghausen from similar stocks. As a test of both the method and the technic, an uncured di-*o*-tolylguanidine tread stock was analyzed, since it was believed that, in this case, an effective procedure should account for substantially all of the guanidine put into the stock. The result was that little or no more guanidine was recovered from the uncured stock than from the same stock at an optimum cure. Guanidine recoveries from either one ranged from 30 to 50 per cent.

To find the reason why the guanidine could not be completely extracted from the uncured mixture, the procedure was applied to a series of stocks in which the ingredients of the original tread stock were omitted, one by one. Finally, it was found that when a simple mixture of acetone-extracted rubber and di-*o*-tolylguanidine was extracted with acetone, a part of the di-*o*-tolylguanidine, amounting to 0.2 to 0.4 per cent of the guanidine on the rubber, was unextractable. Apparently

the di-*o*-tolylguanidine was bound by, or formed a compound with, the rubber and/or the nonextractable protein of crude rubber. It was already known, however, that if a mixture of rubber and guanidine is swollen in a rubber solvent and shaken with dilute acid, all the guanidine is transferred to the aqueous phase wherein it can be determined as the picrate or by back-titration with alkali. Accelerator master batches have been analyzed by such a procedure for some time.

Thus, it seemed probable that, if all the guanidine could be recovered from an uncured mix by such a method, whereas it could not be completely recovered by acetone extraction, a higher recovery of guanidine might be obtained from cured stocks by treatment with an aqueous acid and a swelling agent than by acetone extraction. This proved to be the case. The cured di-*o*-tolylguanidine tread, from which only 30 to

TABLE I. STOCKS INVESTIGATED

	Stock A	Stock B
	Parts	Parts
Rubber (crepe)	100	100
Sulfur	3.8	3.8
Thermatomic black	38.3	38.4
D. P. G.	1.44	1.38
Zinc oxide	3.8
	<hr/>	<hr/>
D. P. G. content, %	143.54	147.38
	1.00	0.94
	<hr/>	<hr/>
	Stock C	Stock D
Rubber (smoked sheet)	100	100
Sulfur	2.8	2.8
Zinc oxide	6.6	6.6
Rubber channel black	46.2	46
Stearic acid	3.3	3.3
Pine tar	3.9	3.9
Antioxidant ^a	1.0	1.0
Accelerator	1.04 (D. P. G.)	0.82 (D. O. T. G.)
	<hr/>	<hr/>
D. P. G. content, %	164.84	164.42
D. O. T. G. content	0.63	0.50

^a 92.5 per cent phenyl- α -naphthylamine, 7.5 per cent *m*-toluylene diamine.

50 per cent of the guanidine could be recovered by acetone extraction, yielded 75 per cent or more of the original amount of guanidine when a method involving treatment with benzene and dilute acid was used. The increased amount of guanidine was obtained by the latter method because of the hydrolyzing action of the aqueous acid rather than the swelling action of benzene. This was shown by extracting the cured tread with benzene and then shaking the benzene extract solution with dilute acid. The amount of guanidine recovered in this way was essentially equal to that obtained by extraction with dry acetone. Furthermore, extraction with wet acetone removed much more guanidine from the stock than extraction with dry acetone, although a 20-hour extraction with acetone containing 2 per cent of water did not effect as high a recovery of guanidine as could be obtained with benzene and aqueous acid. It was also found that the guanidine recovery was highly variable if, when the Wistinghausen procedure was

followed, the acetone extractions were run without particular attention to keeping the acetone absolutely dry.

A brief study of the apparent consumption of guanidine during cure was made, using both Wistinghausen's method and the new method, which yields a higher guanidine recovery from a cured stock and complete recovery from an uncured stock. A comparison of the accelerator consumption curves obtained by the two different methods is presented.

Four different stocks were investigated, A, B, C, and D. Stocks A and B are duplications of two stocks used by Wistinghausen. Stocks C and D are present-day tread compounds, the former containing diphenylguanidine, the latter di-*o*-tolylguanidine.

Each stock was cured 10, 30, 60, and 90 minutes at 307° F. (152° C.). Stock C was also cured 30, 60, 90, and 120 minutes at 290° F. (143° C.). Much of the preliminary work was done on stock D, cured 90 minutes at 290° F. (143° C.).

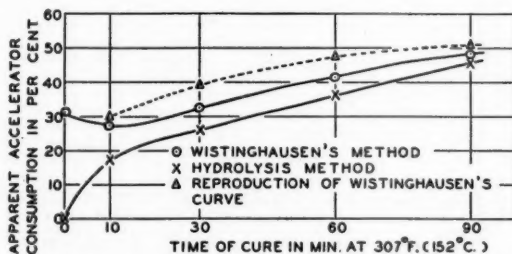


FIGURE 1. ACCELERATOR CONSUMPTION IN A Wistinghausen's base stock

Most of the other cures were beyond the optimum, as far as desirable physical properties are concerned. For the stocks cured at 307° F. (152° C.) the optimum time is probably about 25 minutes, while for those cured at 290° F. (143° C.) the optimum time is about 90 minutes.

In preparation for analysis, the stock, where possible, was finely ground to "springs" on a cold mill. Uncured or under-cured stocks that could not be crumbled were sheeted as thinly as possible and cut into small pieces.

The procedure used for the analysis of the stocks by the acetone-extraction method varied slightly but not essentially from that described by Wistinghausen. This slight modification of the Wistinghausen method and the new method involving hydrolysis are described below.

Method of Analysis

WISTINGHAUSEN METHOD. A 20-gram sample of the stock is extracted with acetone for 16 hours in a Soxhlet extraction apparatus. The acetone is completely removed from the extract by evaporation and the residue is dissolved in 20 cc. of ether.

Thirty cubic centimeters of approximately 0.1 *N* hydrochloric acid are added to the solution and the mixture is heated on the steam plate for 5 or 10 minutes longer than is required to evaporate the ether. The hot aqueous solution is then poured through a filter. This treatment with ether and hot dilute acid is repeated twice to transfer all the guanidine to the aqueous acid solution which is allowed to stand at least 12 hours and then again filtered cold. The volume is adjusted to approximately 100 cc. and an equal volume of saturated aqueous picric acid solution is added. This mixture is heated on the steam plate for 1 hour. Heating causes the precipitate that first forms to redissolve.

The heating period was found to be particularly necessary for di-*o*-tolylguanidine determinations, as di-*o*-tolylguanidine picrate forms slowly and incompletely in the cold. On cooling and standing, the diphenylguanidine picrate usually reprecipitates in crystalline form, but the di-*o*-tolylguanidine picrate

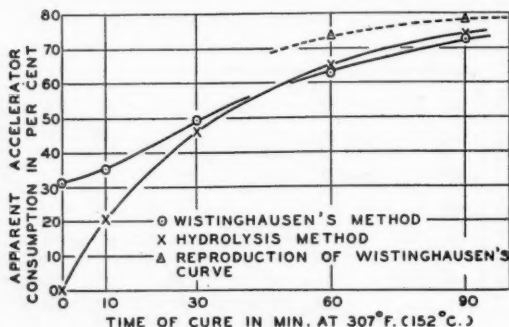


FIGURE 2. ACCELERATOR CONSUMPTION IN B
Wistinghausen's 3.8 per cent zinc oxide stock

only infrequently reprecipitates in this way. The precipitate should be allowed to stand for at least 12 hours before filtering. For di-*o*-tolylguanidine, especially, a longer period (48 hours) seems to help the character and quality of the precipitate. The filtration is carried out on a Gooch crucible lined with filter paper, the precipitate being completely transferred to the crucible with the aid of a "policeman" and a small amount of water. The precipitate is finally dried to constant weight in a 100° to 110° C. oven. An addition of 5 mg. is made to the weight of the picrate in the case of the di-*o*-tolylguanidine picrate and 8 mg. in the case of the diphenylguanidine picrate to correct for the slight solubility of these picrates in the 200-cc. mixture of saturated picric acid solution and 0.1 *N* acid. These solubility corrections were obtained from direct determinations of the solubility of the pure picrates in such a mixture at room temperature. For diphenylguanidine, the amount of guanidine is 48 per cent of the corrected weight of the picrate and for di-*o*-tolylguanidine, 51 per cent of the corrected weight of its picrate.

HYDROLYSIS METHOD. A 20.0-gram sample of the finely divided stock, 400 cc. of benzene, and 50 cc. of approximately 0.1 *N* hydrochloric acid are placed in a 1-liter flask so arranged that constant agitation of the mixture and refluxing of the benzene can be carried out together and the aqueous layer can be conveniently removed from the rest of the mixture, preferably without removing the whole mixture from the flask. A convenient apparatus for this purpose is a 1-liter Erlenmeyer flask to which has been sealed, near the base and projecting to the side, a stopcock outlet. By means of an ordinary addition tube placed in the neck with a cork stopper, the flask can be equipped with a stirrer and a reflux condenser. No mercury seal is necessary. The flask is heated, conveniently, by means of an electric hot plate.

Refluxing and brisk stirring of the mixture are continued for 1 hour. The condenser and stirrer are then removed, the flask is set on its side in a tripod, and the aqueous layer drawn off.

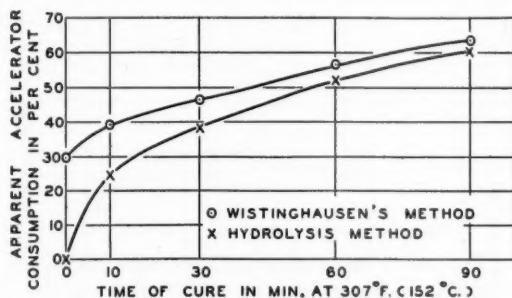


FIGURE 3. ACCELERATOR CONSUMPTION IN C
Diphenylguanidine tread stock, cured at 307° F. (152° C.)

At the temperature of refluxing benzene, little or no emulsification takes place. Another 50-cc. portion of dilute acid is added and the procedure is repeated. After a third similar treatment with acid, all the recoverable guanidine in the stock has been removed by the acid. The combined acid solution is allowed to cool completely and is then filtered. The filtered solution is clear and usually slightly yellow. The volume is adjusted by evaporation to about 100 cc. and an equal volume of saturated aqueous picric acid solution is added. The rest of the procedure is identical with that described above for the Wistinghausen method.

Besides the fact that it yields higher recoveries of guanidine through hydrolytic splitting of the bound guanidine complex, the hydrolysis method possesses several advantages as an analytical method over the Wistinghausen method. The quality of the picrates is much better, especially in di-*o*-tolylguanidine determinations. In the Wistinghausen method, picrates are frequently obtained which are noncrystalline, dark brown, and melt 20° C. lower than that of the pure picrate, whereas in the present method they are always crystalline, bright yellow, and seldom melt more than 6° C. lower than the pure picrate. Because the picrates obtained are purer and because the variability introduced by different moisture contents in the acetone extractions in the Wisting-

hausen procedure is not present, the results obtained by the hydrolysis method usually check much better than those obtained by the Wistinghausen method as used in this laboratory. For qualitative purposes only, the hydrolysis method is very rapid, a half hour's stirring and refluxing being sufficient to remove the greater portion of the guanidine. A qualitative determination requires only 2 or 3 hours' time from the beginning of the determination to obtaining the characterizing melting point of the picrate.

The modification of the above method to determine the guanidine in an uncured stock by precipitation as the picrate is as follows:

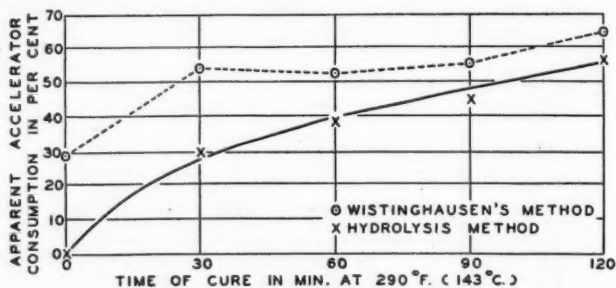


FIGURE 4. ACCELERATOR CONSUMPTION IN C
Diphenylguanidine tread stock, cured at 290° F. (143° C.)

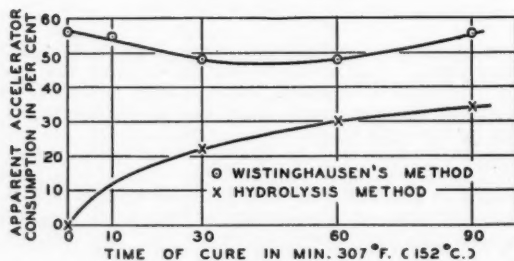


FIGURE 5. ACCELERATOR CONSUMPTION IN D
Di-*o*-tolylguanidine tread stock

A 10.0-gram sample is dissolved in 400 cc. of benzene by means of stirring and heating. If small bits of incompletely dispersed stock persist in the cement, no harm is done. Fifty cubic centimeters of approximately 0.1 *N* hydrochloric acid and 50 cc. of water are added and the mixture is stirred and heated for 20 to 30 minutes. The benzene is then evaporated while stirring is continued. When evaporation is complete, the rubber remains in a porous, spongy mass in the aqueous solution. The latter, containing most of the guanidine, is poured off. The remaining traces of guanidine can be removed from the stock by digesting for a few minutes with each of two more successive 50-cc. portions of 0.1 *N* acid. The procedure is then continued as described above.

TABLE II. PRELIMINARY RESULTS

Deter- mination No.	Stock	Method	Wt. of Picrate		A. V. Wt. of Picrate Corrected for Solubility	Accelerator Recovered % ^c	Apparent Acceler- ator Con- sumption % ^d	M. P. of Picrate ° C.	Remarks
			A Mg.	B Mg.					
29	D. P. G. (50 mg., commercial)	...	94.1	95.1	102.6	98.7	..	163-5°	Theoretical wt. of picrate, 104.0 mg.
1	D. O. T. G. (50 mg., pure)	...	93.2	93.0	98.1	100.0	..	158-60	Theoretical wt. of picrate 98.0 mg.
2	D. O. T. G. (50 mg., commercial)	H ^d	91.1	91.3	96.2	98.2	24	158-60	Three 1-hr. periods
3	D. ^e	H	144.3	145.4	150.0	76	Three 2-hr. periods
7	D.	H	143.2	138.3	Three 8-hr. periods
10	D.	H	132.2	138.5	Commercial acetone
11	D.	W ^e	123.9	124.7	130 ^e	66 ^e	34	..	Dry c. p. acetone
12	D.	W	86.3	86.0	91	46	54	..	Commercial acetone + 10% water
14	D.	W	113.5	117.4	Commercial acetone + 2% water
9	D.	...	127.9	127.3	Benzene extraction
			80.0	78.8	84	43	57	..	

^a The m. p. of diphenylguanidine picrate is 170° C.; of di-*o*-tolylgani-
dine picrate, 162-3° C.

^b Cured 90 minutes at 290° F. (143° C.).

^c Theoretical amount of guanidine picrate for D, 106 mg.

^d Hydrolysis method.

^e Wistinghausen method.

Analytical Data

The analytical results given in Tables II and III are largely self-explanatory. Table II covers the preliminary work.

In the first three tabulated determinations (Nos. 29, 1, and 2), the uncompound guanidines, dissolved in 100 cc. of 0.1 *N* hydrochloric acid, were precipitated with an equal volume of picric acid solution to check the completeness of the precipitation. When the 5- and 8-mg. corrections for solubility were added to the weights of the picrates obtained, the results were satisfactory. The next three determinations (Nos. 3, 5, and 7) were run to gain some idea as to the proper length of time for the extraction period in the hydrolysis method. It was concluded that there was no reason for continuing these extraction periods for longer than an hour. The next four determinations (Nos. 10, 11, 12, and 14) were made, employing various acetone extraction procedures as indicated under "Remarks," and show the variation in results caused by the introduction of water. The last determination (No. 9) was run by extracting the stock with dry benzene and then determining the guanidine in the filtered extract by hydrochloric acid extraction and precipitation in the usual manner.

Since the results obtained were substantially the same as those obtained with dry acetone, it is evident that the acetone-insoluble guanidine in the stock is liberated by the hydrolytic effect of the acid rather than by the swelling effect of the benzene.

Table III is a tabulation of the results obtained on the various cures of stocks A, B, C, and D. The curves shown in Figures 1 to 5, inclusive, were obtained by plotting the apparent accelerator consumption—i. e., the difference between the theoretical and the determined value—against the time of cure. Figures 1 and 2 also contain a reproduction of Wistinghausen's curves for stocks A and B, which are inserted for the sake of comparison. In Figure 4, no reasonable curve representing accelerator consumption as determined by the Wistinghausen method can be drawn through the plotted points.

It will be necessary to obtain further data, especially for short curing periods, in order to determine the true course of the curve.

Discussion of Results

Reference to Figures 1, 2, and 3 shows that, for diphenylguanidine stocks, the curves obtained by the hydrolysis and Wistinghausen methods are approximately identical over the greater part of their range. From this it might be inferred that, for practical purposes, the guanidine could be determined by either method. This would be true if we were interested in overcured stocks, but it should be recalled that, for commercial stocks, only the first quarter of the curves (Figures 1, 2, or 3) would be involved. Figure 4 (diphenylguanidine stock cured at 290° F., 143° C.) shows the situation

TABLE III. ANALYTICAL DATA

Determination No.	Stock	Cure		Method	A		B		A ^a , Wt. of Picrate Corrected for Solubility	Accelerator Recovered	Apparent Accelerator Consumption		M. P. of Picrate °C.
		Time Min.	Temp. °F.		Mg.	Wt. of Picrate	Mg.	%			%		
65	A ^a	0	307	W	269.6	289.9	289.9	287	69	31	158-61 ^b		
47	A	10	307	W	296.3	296.4	296.4	304	73	27	153-5		
48	A	30	307	W	273.1	268.4	268.4	279	67	33	153-5		
49	A	60	307	W	234.3	237.9	237.9	244	58	42	152-4		
60	A	90	307	W	208.7	209.2	209.2	217	52	48	152-4		
34	A	10	307	H	338.1	336.9	336.9	306	83	17	153-5		
23	A	30	307	H	301.4	302.4	302.4	310	74	26	152-4		
24	A	60	307	H	255.7	254.9	254.9	263	63	37	152-4		
25	A	90	307	H	219.3	217.6	217.6	226	54	46	150-2		
66	B ^a	0	307	W	265.0	239.2	239.2	255	65	35	151-4		
43	B	10	307	W	255.5	239.2	239.2	255	65	35	151-4		
45	B	30	307	W	193.0	188.8	188.8	199	51	49	157-60		
44	B	60	307	W	135.4	136.9	136.9	144	37	63	151-5		
46	B	90	307	W	94.7	96.2	96.2	103	27	73	154-7		
26	B	10	307	H	299.1	296.0	296.0	306	79	21	152-5		
27	B	30	307	H	204.9	203.3	203.3	212	64	46	152-5		
28	B	60	307	H	131.1	128.3	128.3	138	35	65	152-4		
31	B	90	307	H	90.0	93.7	93.7	100	26	74	150-3		
64	C ^d	0	307	W	182.7	174.6	174.6	186	71	29	158-61		
51	C	10	307	W	152.7	151.7	151.7	161	61	39	150-3		
52	C	30	307	W	132.5	134.2	134.2	141	64	46	151-4		
53	C	60	307	W	112.8	101.7	101.7	115	44	66	155-9		
54	C	90	307	W	86.6	88.9	88.9	96	37	83	150-2		
63	C ^f	0	307	H	123.0	119.0	119.0	129	99	1	154-6		
39	C	10	307	H	185.7	185.0	185.0	195	75	25	152-4		
40	C	30	307	H	157.9	152.4	152.4	163	62	38	151-3		
38	C	60	307	H	117.7	119.9	119.9	127	48	62	151-3		
37	C	90	307	H	96.2	90.3	90.3	104	40	60	150-3		
64	C	0	290	W	182.7	174.6	174.6	186	71	29	158-61		
60	C	30	290	W	111.4	113.5	113.5	120	48	54	152-4		
61	C	60	290	W	112.1	112.7	112.7	125	45	52	152-4		
62	C	90	290	W	118.0	103.2	103.2	118	37	63	152-4		
69	C	120	290	W	92.4	86.3	86.3	98	32	68	151-4		
19	C ^f	0	290	H	122.3	119.0	119.0	129	79	30	152-4		
19	C	30	290	H	174.6	173.1	173.1	182	62	38	152-4		
17	C	60	290	H	159.4	153.8	153.8	163	52	45	152-4		
21	C	90	290	H	138.3	132.6	132.6	143	44	50	152-4		
21	C	120	290	H	108.3	108.9	108.9	114	44	50	152-4		
67	D ^a	0	307	W	78.2	82.5	82.5	85	45	57	151-6		
57	D	10	307	W	81.5	83.9	83.9	88	45	55	151-6		
58	D	30	307	W	96.8	90.0	90.0	102	52	48	151-6		
55	D	60	307	W	103.6	90.5	90.5	89	45	48	151-6		
56	D	90	307	W	76.9	78.9	78.9	89	45	55	151-5		
36	D	30	307	H	146.9	146.9	146.9	152	22	30	158-60		
41	D	60	307	H	131.6	134.1	134.1	138	70	30	158-60		
42	D	90	307	H	122.1	125.5	125.5	129	66	34	158-60		

^a Theoretical amount of guanidine picrate, 417 mg.

^b The m. p. of diphenylguanidine picrate is 170° C.; of di-*o*-tolylguanidine picrate, 162-3° C.

^c Theoretical amount of guanidine picrate, 390 mg.

^d Theoretical amount of guanidine picrate, 262 mg.

^e Theoretical amount of guanidine picrate, 196 mg.

^f 10.0 gram sample.

in the range of the optimum cure somewhat better, as far as distance between the curves is concerned, although the true course of the Wistinghausen curve is not known. In the case of di-*o*-tolylguanidine stocks (see Figure 5), the difference between the two curves is much more pronounced. There is apparently more extensive compound formation with di-*o*-tolylguanidine than with diphenylguanidine and this addition compound of di-*o*-tolylguanidine is less readily destroyed. This behavior may be the cause of the greater accelerating activity of di-*o*-tolylguanidine as compared to diphenylguanidine.

The present investigation has raised a number of questions which can be answered only by further research. Among other things, the probability that there is compound formation between the guanidine and the protein, or the rubber, is extremely interesting. The fact that the curves as determined by the acetone-extraction method and by the hydrolysis method approach each other as the cure continues indicates that it is the bound guanidine that is being destroyed. It seems quite possible that the greater part of the accelerating effect on vulcanization is not due to the guanidine itself but to an addition product of guanidine and an ingredient of crude rubber. In any case, the author believes that further work in this direction will throw considerable light on the mechanism of acceleration.

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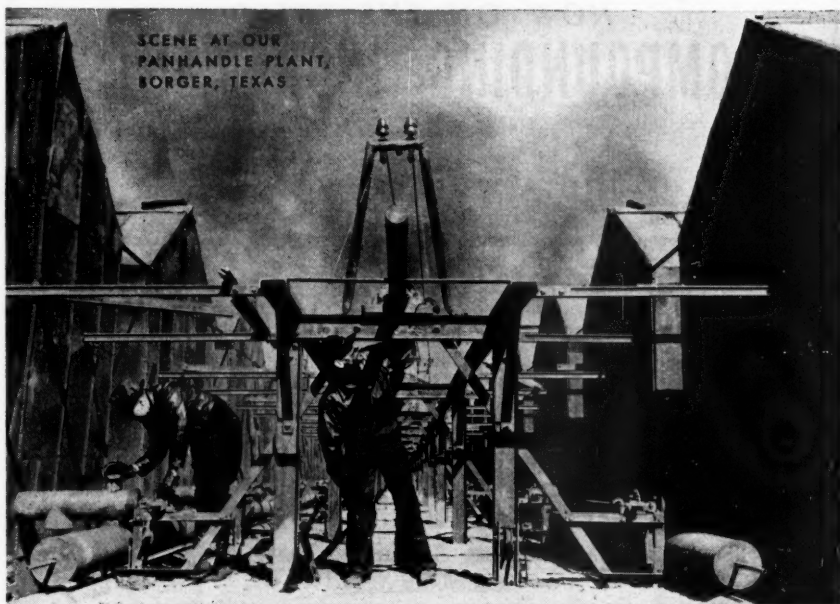
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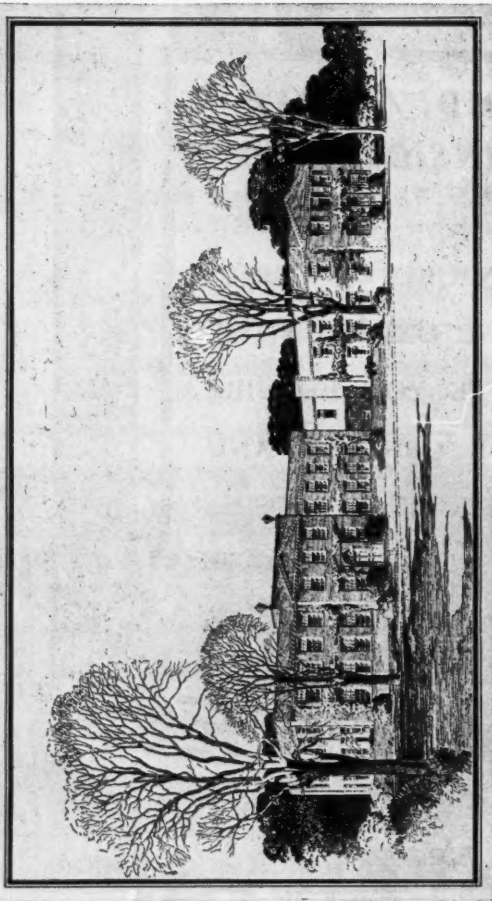
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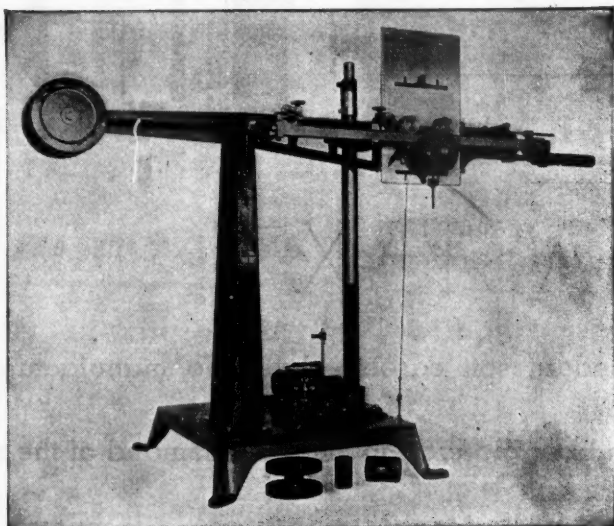
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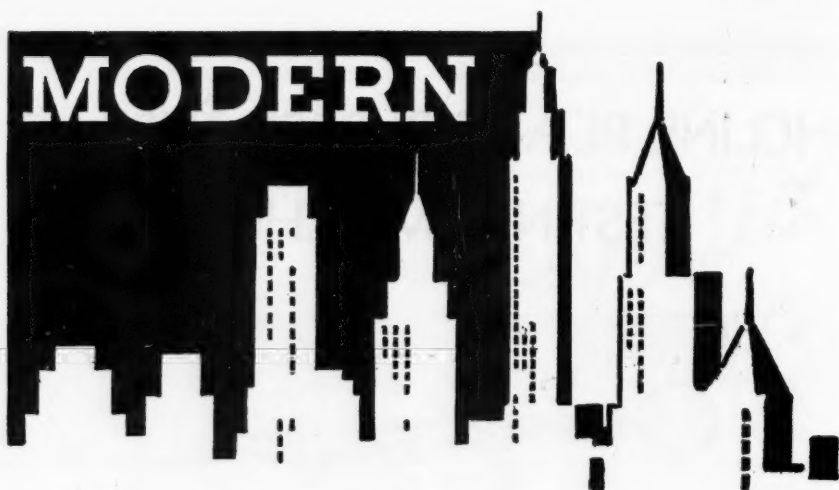
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